# SYNTHESES OF POLYFUNCTIONAL CYCLOPROPANES

Thesis for the Degree of Ph. D.

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Yoon Chin Kim

1965

This is to certify that the

thesis entitled

SYNTHESES OF POLYFUNCTIONAL CYCLOPROPANES

presented by

Yoon Chin Kim

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Harold Hart
Major professor

Date September 21, 1965

ABSTRACT

SYNTHESES OF POLYFUNCTIONAL CYCLOPROPANES

by Yoon Chin Kim

Non-catalyzed condensation of the systems RR'C=CAB (I, R, R' = H, alkyl, aryl; A, B = CN, $COOC_2H_5$, $CONH_2$) and CHBrYZ (II, Y, Z = CN, $COOC_2H_5$, $CONH_2$) produced the corresponding polyfunctional cyclopropanes (III, CRR'CABCYZ).

Condensation of alkylidenemalononitrile (I, R, R' = alkyl; A = B = CN) and bromomalononitrile (II, Y = Z = CN) produced 3,3-dialkyl-1,1,2,2-tetracyanocyclopropanes (III, R, R' = alkyl; A = B = Y = Z = CN). The reaction appeared to be influenced by steric and electronic effects of the alkylidenemalononitriles. 3,3-Dicyclopropyl-, 3-ethyl-3-n-butyl-, 3,3-nonamethylene-, 3,3-undecamethylene-, and 3,3-tetradecamethylene-1,1,2,2-tetracyanocyclopropanes which previously failed to form by the original Wideqvist reaction (from the corresponding ketones and bromomalononitrile in the presence of the iodide ion) were produced by the present method.

A number of 3-aryl-1,1,2,2-tetracyanocyclopropanes (III, R = H; R' = phenyl or substituted phenyl; A=B=Y=Z=CN) were prepared from arylidenemalononitriles (I, R = H; R' = phenyl or substituted phenyl; A = B = CN)and bromomalononitrile. Introduction of an electron-withdrawing group into the benzene ring did not seem to particularly facilitate the reaction. However, introduction of an electron-releasing group did slow down the reaction. The cyclopropyl hydrogen of a number of 3-aryl-1,1,2,2-tetracyanocyclopropanes were shown, in the NMR spectra, to couple to the ortho hydrogens of the

phenyl group (four bonds away) with coupling constants ranging between 0.6 c.p.s. and 1.0 c.p.s.

Some 3,3-dialkyl-2-carbethoxy-1,1,2-tricyanocyclopropanes (III, R,R' = alkyl; A = $COOC_2H_5$; B = Y = Z = CN) and 3-aryl-2-carbethoxy-1,1,2-tricyanocyclopropanes (III, R = H; R' = phenyl or substituted phenyl; A = $COOC_2H_5$; B = Y = Z = CN) were prepared by the following two routes: (i) Ethyl alkylidene- or arylidenecyanoacetates (I, R, R' = H, alkyl, phenyl or substituted phenyl) and bromomalononitrile and (ii) alkylidene- or arylidenemalononitriles and ethyl bromocyanoacetate (II, Y = CN; Z = $COOC_2H_5$). Route (i) appeared to be superior to route (ii), since it produced a larger number of compounds quicker and in better yield than route (ii). Stereoisomers of these compounds were studied by NMR spectra. 3-Methyl-3-i-propyl, 3-phenyl-, and 3-p-methoxyphenyl-2-carbethoxy-1,1,2-tricyanocyclopropane were shown to be produced as single stereoisomers in which the i-propyl, phenyl, or p-methoxyphenyl group is trans to the carbethoxyl group.

A few derivatives of 2-carboxamido-1,1,2-tricyanocyclopropanes (III, R,R' = H, alkyl, phenyl, or substituted phenyl; A = $CONH_2$; B = Y = Z = CN), on boiling in methanol or ethanol, readily cyclized to form the corresponding derivatives of 1,5-dicyano-2-imino-3-aza-4-ketobicyclo[3.1.0]hexanes. The acid treatment of these bicyclo[3.1.0]hexanes produced the corresponding 1,2-dicyano-1,2-carboximidocyclopropanes.

Dimers of isopropylidenemalononitrile, 2-butylidenemalononitrile, and cyclopentylidenemalononitrile were prepared by treating the corresponding monomers with pyridine. They were also obtained as by-products while preparing the monomers.

2,3-Benzocyclohexylidenemalononitrile and 2,3-benzocyclopentylidenemalononitrile, on refluxing with bromomalononitrile, produced 2-bromo-1-dicyanomethylenetetralin and an unidentified compound $C_{12}H_6Br_2N_2$, respectively. 2,3-Benzocyclohexylidenemalononitrile was found to condense with bromomalononitrile, in 80% aqueous ethanol and at room temperature, to form spiro[2,2,3,3-tetracyanocyclopropane-1,1'-tetralin].

Reaction of bromomalononitrile with ethanol produced 1,1-dicyano-2-amino-2-ethoxyethylene. Reaction of bromomalonitrile with 1-nitro-2-methylpropene gave 3-(2'-bromo-2'-propyl)-1,1,2,2-tetracyanocyclopropane and an unidentified compound $C_7H_8N_4O_3$.

Reaction of ethyl sodiocyanoacetate with bromine in carbon tetrachloride produced 1,2,3-tricarbethoxy-1,2,3-tricyanocyclopropane and the reaction of ethyl sodiocyanoacetate with bromine in carbon disulfide formed compound $C_{12}H_{10}N_2O_4S_3$ which was tentatively identified as 3,5-bis(cyanocarbethoxymethylene)-1,2,4-trithiacyclopentane.

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To my Father and in
memory of my Mother

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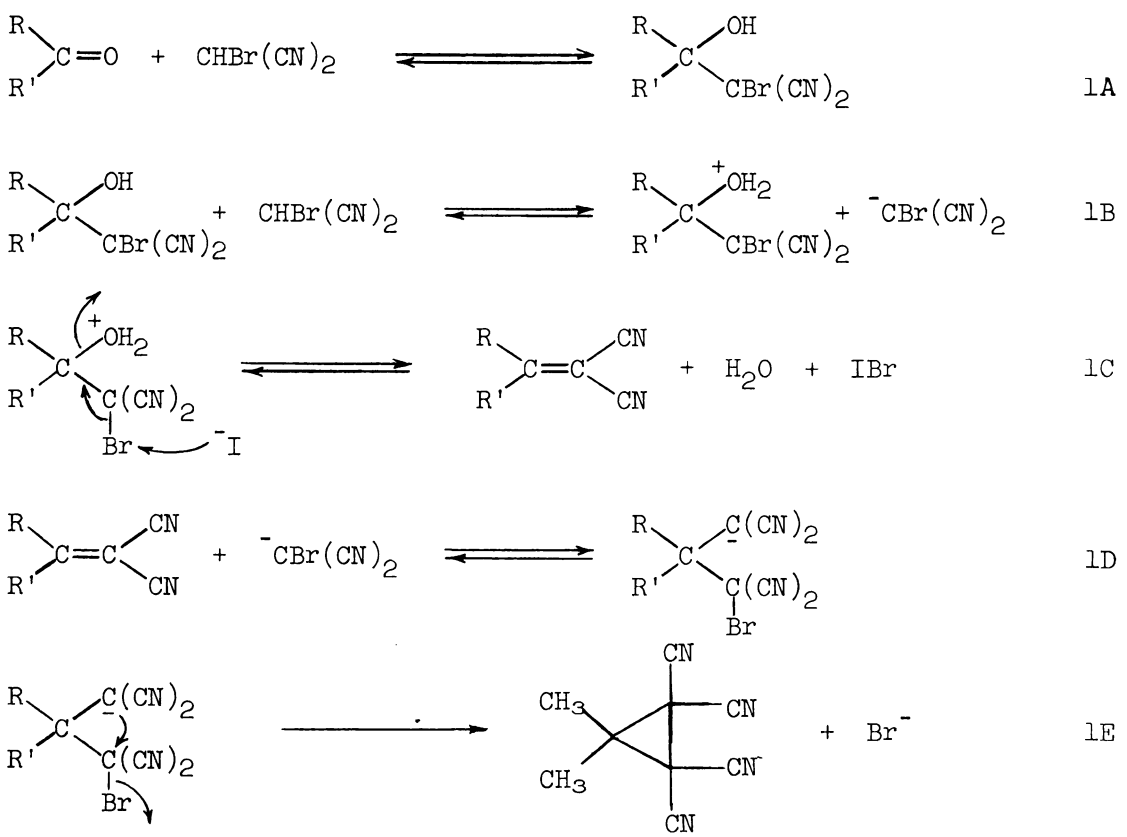
# INTRODUCTION

Wideqvist and Ramberg obtained a crystalline compound, identified as 3,3-dimethyl-1,1,2,2-tetracyanocyclopropane, by treating acetone with two moles of bromomalononitrile in the presence of aqueous potassium iodide (1). This reaction, which now is known as Wideqvist Reaction (2), was soon extended to several different carbonyl compounds (ketones and aldehydes) to prepare the appropriately substituted 1,1,2,2-tetracyanocyclopropanes (3).

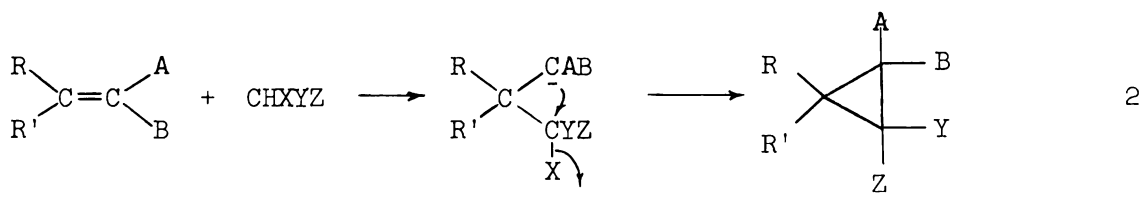
Recently, the scope of the Wideqvist reaction was extensively studied and the following mechanism for the formation of the tetracyanocyclopropanes was proposed (4).



Bromomalononitrile, with $pK_a$ of approximately 5 (5), is probably acidic enough to protonate the carbonyl oxygen for the initial condensation (step 1A-C). The ease with which alkylidenemalononitrile is formed (step 1A-C) may be a primary factor for determining the success of the Wideqvist reaction. Once the alkylidenemalononitrile is formed, it may react further with bromomalononitrile in an irreversible process to yield the product, provided there are no unfavorable steric or electronic effects.

Step 1D is especially significant because, if this reaction proceeds through formation of an alkylidenemalononitrile, then it should be possible to prepare 1,1,2,2-tetracyanocyclopropanes from equimolar amounts of alkylidenemalononitriles and bromomalononitrile without using iodide ion. If cyclopropanes could be formed directly from alkylidenemalononitriles and bromomalonitrile, this would lend support to the foregoing mechanism.

Another significance of step 1D lies in a possible generalization of this reaction as shown in the following equation, where A, B, Y, and Z are




2

electron-withdrawing groups such as -CN, -COOR, $-CONH_2$, $-NO_2$, $-SO_2R$, etc. and X is a leaving group such as -Cl, -Br, -I, -OTs, etc. This reaction scheme would make it possible to replace one or more of the cyano groups of 1,1,2,2-tetracyanocyclopropanes by some other electron-withdrawing group(s), if properly substituted reactants were used.

This thesis describes mainly the syntheses of substituted polyfunctional cyclopropanes according to the above scheme. The reactant pairs that have

been used for this study are as follows:

i. A = B = Y = Z = CN; X = Br

ii. A = $COOC_2H_5$; B = Y = Z = CN; X = Br

iii. A = B = Y = CN; Z = $COOC_2H_5$; X = Br

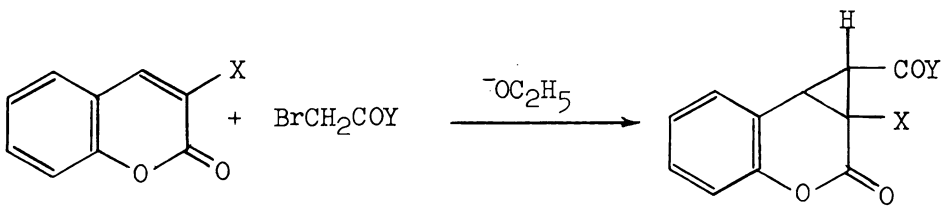
iv. A = $CONH_2$; B = Y = Z = CN; X = Br

v. A = B = Y = CN; Z = $CONH_2$; X = Br

## HISTORICAL

Polyfunctional cyclopropanes are often prepared by the base catalyzed condensation of an activated $\alpha,\beta$-unsaturated system with $\alpha$-halo esters, ketones, nitriles, etc. followed by an intramolecular dehydrohalogenation. The present work involves a similar type of reaction, except that base is not used as a catalyst. In this connection, it would be worthwhile to discuss some of the previous work.

Widman (6,7) obtained 3-acetyl-3,4-phenacylidenecoumarin (III, X = $COCH_3$, Y = $C_6H_5$) by reacting 3-acetylcoumarin (I, X = $COCH_3$) with phenacyl bromide (II, Y = $C_6H_5$) in the presence of sodium ethoxide. The reaction was extended to prepare several analogs by substituting



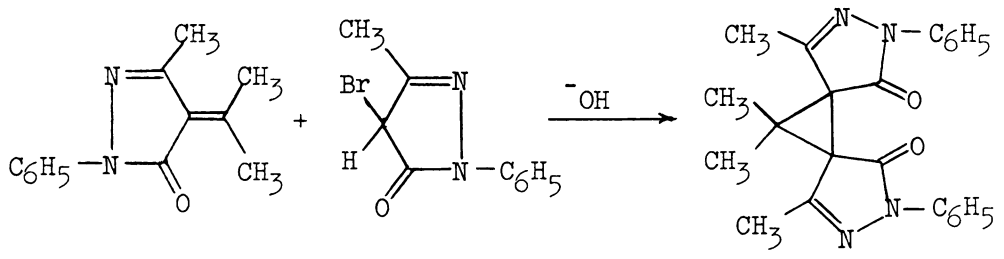

I II III 3

X=$COCH_3$, $COOC_2H_5$, CN; Y=$C_6H_5$, p-$CH_3OC_6H_4$, m-$O_2NC_6H_4$, $\alpha$-Naphthyl

various groups for X and Y.

Fraisse and co-workers condensed diethyl bromomalonate with ethyl acrylate and acrylonitrile using sodium ethoxide and obtained the corresponding cyclopropanes (8). They also carried out further condensations of various substituted acrylic esters and $\alpha$-halo esters or $\alpha$-halo nitriles (9, 10, 11, 12).

Westoo obtained compound VI by reacting 1-phenyl-3-methyl-4-bromo-2-pyrazoline-5-one (V) with 1-phenyl-3-methyl-4-isopropylidene-2-pyrazoline-5-one (IV) in the presence of sodium hydroxide (13).



IV V VI

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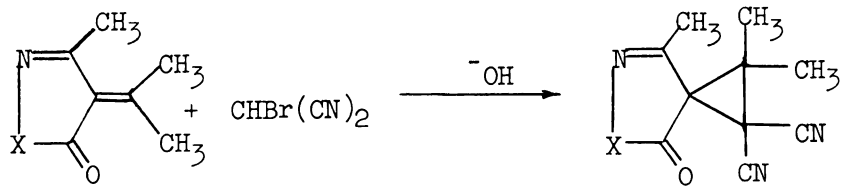
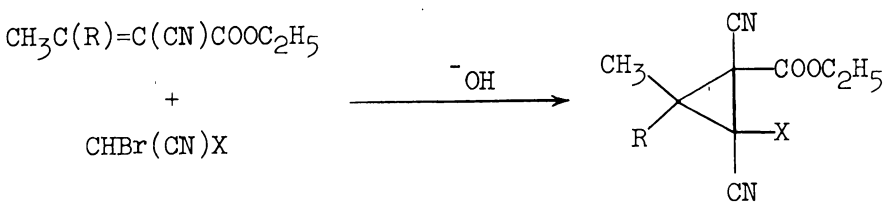
Bromomalononitrile and bromocyanoacetamide were condensed to activated $\alpha,\beta$-unsaturated system with sodium hydroxide to form the appropriately substituted cyclopropanes (14, 15).



X=O, $C_6H_5N$

5*



$R=CH_3$, $C_2H_5$; $X=CN$

$R=CH_3$ ; $X=CONH_2$

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Warner reacted $\alpha,\beta$-unsaturated aldehydes or ketones with diethyl bromomalonate in the presence of sodium ethoxide and obtained the corresponding cyclopropane derivatives (16).

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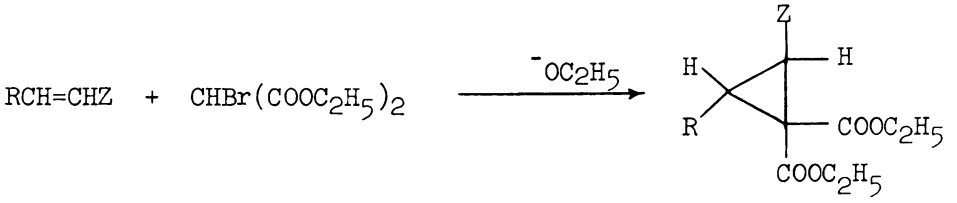
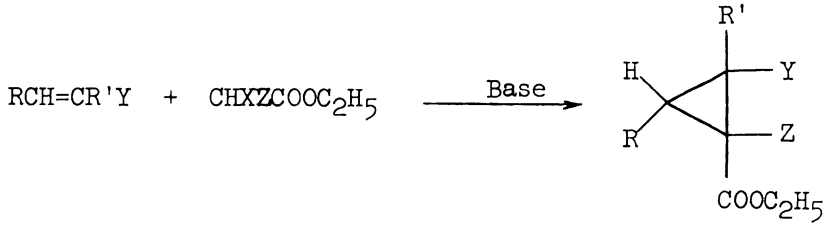
* Use of base was not indicated for the reaction of 3-methyl-4-isopropylidene-2-isoxazoline-5-one (X = O) and bromomalononitrile.




7

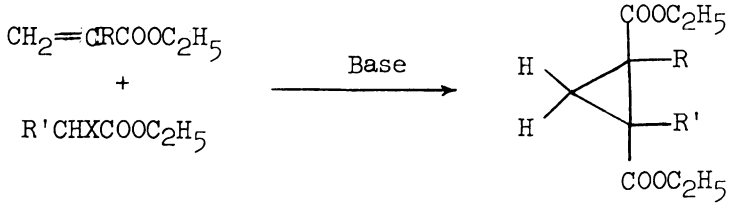
R=H, $CH_3$; Z=CHO, $CH_3CO$

Mousseron and co-workers made an extensive study on the synthesis of polyfunctional cyclopropanes by base condensation of an $\alpha,\beta$-unsaturated system with $\alpha$-halo esters (17, 18, 19). Two representative reactions employed are shown below.




8

R=H, $CH_3$, $COOC_2H_5$; R'=H, $CH_3$; X=Cl, Br; Y=$COOC_2H_5$, CHO, CN; Z=H, $COOC_2H_5$

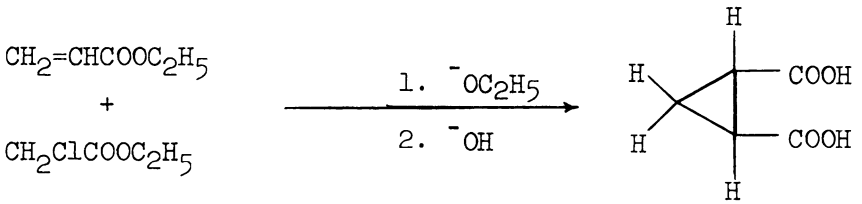



9

R=H, $CH_3$; R'=H, $CH_3$, $C_2H_5$, i-$C_3H_7$; X=Cl, Br, OTs

McCoy studied base condensation of an $\alpha$-halo ester with an $\alpha,\beta$-unsaturated ester to form 1,2-cyclopropanedicarboxylic acid diesters in toluene (20). By saponifying the diesters to the corresponding diacids

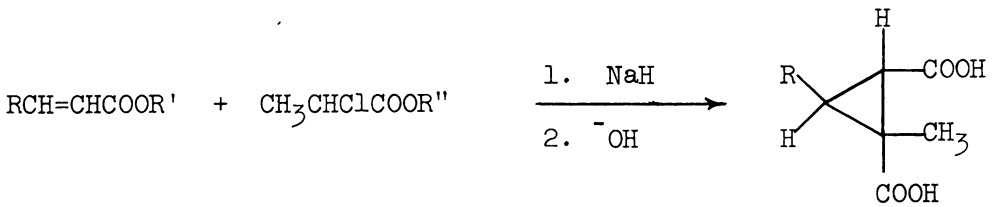
followed by analysis of the stereoisomers, the author found that the less stable cis isomer (cis with respect to two carboxyl groups) was often dominant. For example,




10

Yield 45% (cis, 26%; trans, 22%)

It was also found that α-substituents in either or both of the reacting esters favored the cis isomer, whereas β-substituents in the acrylic ester favored the trans isomers (see Equation 11).

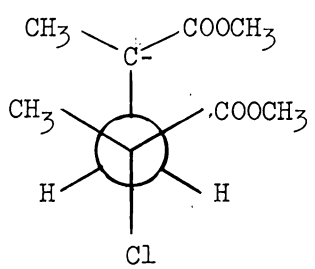



11

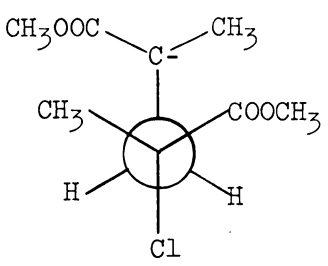
R=H ; R'=$CH_3$ ; R"=$C_2H_5$. Yield 70% (cis, 63%; trans, 14%)
R=$CH_3$; R'=$C_2H_5$; R"=$CH_3$. Yield 65% (cis, ; trans, 66%)

The NaH catalyzed condensation of methyl methacrylate or methacrylonitrile with α-halo esters, nitriles, or ketones showed the same trend of the cis predominance, that is, the isomer in which the activating groups (ester, nitrile, or carbonyl) are cis to each other was predominant or exclusive (21).

This cis dominance was explained as following (22, 23, 24). Consider intermediate anions such as VII or VIII formed by Michael addition of methyl

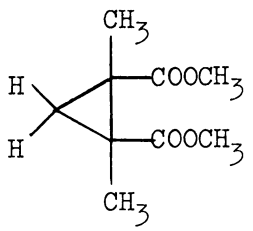



VII




VIII

α-chloropropionate to methyl methacrylate. In solvents of low dielectric constant such as benzene and toluene, intermediate VII would dominate probably because the anion would be better stabilized by interaction with the carbonyl of the second carboxyl group. In this case, the cis isomer would be dominant in the product which was the case. For example,

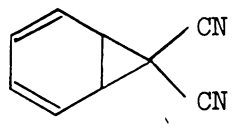


IX

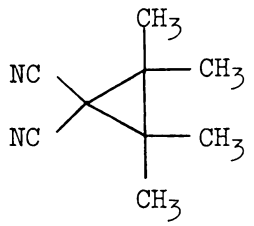
93% of cis-IX was obtained when the reaction was carried out in benzene or toluene. On the other hand, in a medium of high dielectric constant and good solvating properties, intermediate VIII would be dominant. This would be so, because the anion VIII would be not only stabilized by means of external solvation (with solvent) but also would be sterically favored. In this case, the trans isomer would be dominant and this was exemplified by the presence of 66% and 64% of trans-IX in the reaction product, when the reaction was carried out in dimethylformamide or in a 50 : 50 mixture of benzene and hexamethylphosphoramide, respectively.

In the syntheses of cyclopropanes substituted on all three of the ring carbons from properly substituted acrylic ester and α-halo ester, the solvent effect is usually overshadowed by the steric effect (25, 12). However, a fairly high stereospecificity was observed in certain cases. It was also found that an α,β-disubstituted acrylic ester resulted in decreased yields and that a β,β-disubstituted acrylic ester did not yield any isolable product (presumably due to the steric hindrance).

Since the present work is largely concerned with polycyanocyclopropanes, it would be pertinent to mention the recent preparation and reactions of dicyanocarbene. Recently, dicyanocarbene was generated and trapped by benzene (26) and 2,3-dimethyl-2-butene (27) to yield 7,7-dicyanonorcaradiene (X) and 1,1,-dicyano-2,2,3,3-tetramethylcyclopropane (XI).




X

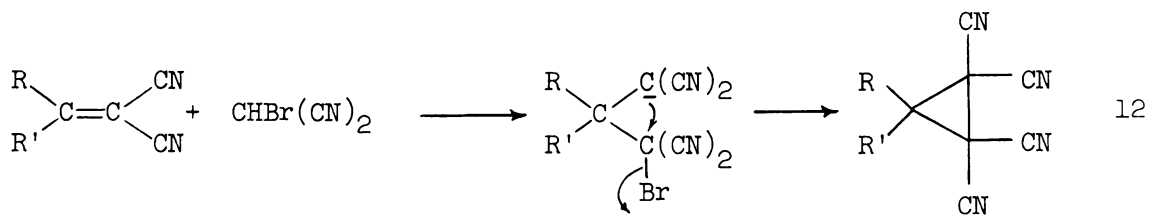



XI

## RESULTS AND DISCUSSION

### A. Reaction of Alkylidenemalononitriles with Bromomalononitrile

For a typical preparation of a 3,3-dialkyl-1,1,2,2-tetracyanocyclopropane, an alkylidenemalononitrile (XII) was allowed to react with an equimolar amount or an excess of bromomalononitrile in aqueous ethanol. The reaction was normally carried out at room temperature and the concentration of ethanol ranged from 50% to 95% depending on the solubility of XII. The mechanism of this reaction, as generally outlined in the introduction involves initial attack of the bromodicyanocarbanion on the β-carbon of XII giving another carbanion XIII, which, by intramolecular displacement of bromide ion, closes the ring.

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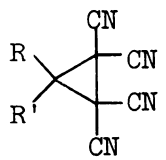
XII XIII XIV

Table 1 lists the tetracyanocyclopropanes which were prepared by this procedure. It includes the yields, and the time elapsed before crystalline product began to separate from the reaction mixture. Although many factors may influence this time interval, these times and yields may give some indication of the ease with which the reaction proceeds. Some comments on the ways in which structural changes in the alkylidenemalononitriles affect the reaction, as judged by these criteria, may be worthwhile.

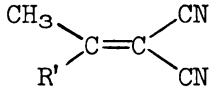
Table 1. 3,3-Dialkyl-1,1,2,2-tetracyanocyclopropanes




| R | R' | Reaction time[a] | Yield, % |
|---|---|---|---|
| $CH_3$ | $CH_3$ | 2-3 mins. | 86 |
| $CH_3$ | $C_2H_5$ | 5-6 mins. | 91 |
| $CH_3$ | n-$C_3H_7$ | 5-6 mins. | 97.5 |
| $CH_3$ | i-$C_3H_7$ | 60 mins. | 97.4 |
| $CH_3$ | t-$C_4H_9$ | b | 0 |
| $CH_3$ | n-$C_5H_{11}$ | 60 mins. | 97.5 |
| $C_2H_5$ | $C_2H_5$ | 2-3 hrs. | 88.5 |
| $C_2H_5$ | n-$C_4H_9$ | 24 hrs. | 94.5 |
| i-$C_3H_7$ | i-$C_3H_7$ | b | 0 |
| i-$C_4H_9$ | i-$C_4H_9$ | b | 0 |
| n-$C_5H_{11}$ | n-$C_5H_{11}$ | b | 0 |
| $(CH_2)_2CH$ | $(CH_2)_2CH$ | 10 mins. | 62 |
| $(CH_2)_4$ | | 30 mins. | 52.6 |
| $(CH_3)CH(CH_2)_2CH(CH_3)$ | | b | 0 |
| $(CH_2)_5$ | | 2-3 mins. | 97.5 |
| $(CH_2)_4CH(CH_3)$ | | 16 hrs. | 39.3 |
| $(CH_2)_9$ | | 15 mins. | 34.8 |
| $(CH_2)_{11}$ | | 60 mins. | 94 |
| $(CH_2)_{14}$ | | 6-7 days | 36[c] |

a. Time elasped before crystalline material began to separate in the reaction mixture.
b. Total reaction time not less than a month.
c. The yield based on the amount of the ketone.

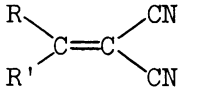
When R of the alkylidenemalononitrile (XII) is methyl, the time necessary to produce product increases rapidly as the R' is changed from methyl to isopropyl, or t-butyl. Despite the fact that the reaction time, when R' = isopropyl, is long, the yield is very high. This was accomplished by adding bromomalononitrile periodically to



| R' = | $CH_3$ | i-$C_3H_7$ | t-$C_4H_9$ | $C_2H_5$ | n-$C_3H_7$ | n-$C_5H_{11}$ |
|---|---|---|---|---|---|---|
| t(min.) = | 2-3 | 60 | (N.R.) | 5-6 | 5-6 | 60 |

the reaction mixture. As will be seen later, bromomalononitrile reacts with the solvent (see page 22). It is therefore necessary to use an additional amount of it especially for a reaction that requires a long reaction time.

When neither of the alkyl groups in the alkylidenemalononitrile (XII) is methyl, the time required for reaction is usually much longer, or the reaction may not occur.



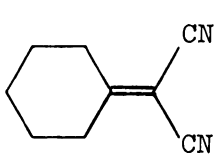
| R = | $C_2H_5$ | $C_2H_5$ | i-$C_3H_7$ | i-$C_4H_7$ |
|---|---|---|---|---|
| R' = | $C_2H_5$ | n-$C_4H_9$ | i-$C_3H_7$ | i-$C_4H_7$ |
| t(hrs.)= | 2-3 | 24 | (N.R.) | (N.R.) |

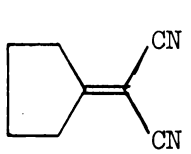
Curiously, when R = R' = cyclopropyl, the reaction is unusually rapid. This is particularly strange, since this reaction fails entirely when carried out as a Wideqvist reaction. That is, 3,3-dicyclopropyl-1,1,2,2-tetracyanocyclopropane could not be obtained directly from dicyclopropyl

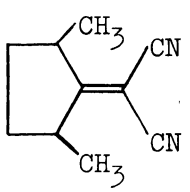
ketone, bromomalononitrile, and iodide ion (28). The reaction does not take place when R = R' = isopropyl. This may be explained in terms of steric and electronic effects. When R = R' = isopropyl, two isopropyl groups certainly will exert a high steric effect against the approaching bromodicyanocarbanion. However, the steric effect of the cyclopropyl is likely to be less than that of the isopropyl, since two methyls are tied back to each other. Besides, the electron-withdrawing inductive effect of the cyclopropyl group is greater than that of the isopropyl group (29). This tends to make the β-carbon of dicyclopropylmethylenemalononitrile more positive relative to that of diisopropylmethylenemalononitrile and thus a better center for the attack of bromodicyanocarbanion.

3-Heptanone failed to produce the cyclopropane product by reacting with bromomalononitrile in the presence of the iodide ion (28). But when 3-heptanone is converted into 3-heptylidenemalononitrile (XII, R = $C_2H_5$, R' = n-$C_4H_9$), then the reaction with bromomalonitrile gave the product, 3-ethyl-3-n-butyl-1,1,2,2-tetracyanoacyclopropane (XIV, R = $C_2H_5$, R' = n-$C_4H_9$). The failure of heptanone and dicyclopropyl ketone to produce the product may be due to the failure of undergoing the initial condensation to form the corresponding alkylidenemalononitriles under the reaction conditions.

In the cyclic alkylidenemalononitriles, their ring size affects the reaction rate and yield. For example, cyclohexylidenemalononitrile gives



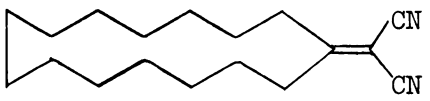



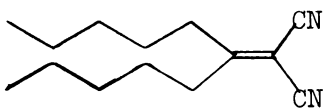

| | | | |
|---|---|---|---|
| T (min.) | = 2-3 | 30 | 30 days |
| Yield (%) | = 97.5 | 52.6 | (N.R.) |

product within a few minutes, whereas cyclopentylidenemalononitrile requires 30 minutes for the formation of the product. This may be explained in terms of internal ring strain and non-bonding interactions (30). Cyclopropanization of the exocyclic double bond involves a change from $sp^2$ to something approaching $sp^3$ hybridization. In case of the cyclohexane ring, this conversion is generally favored because the six-membered ring is least strained when all six carbons are saturated. However, the reverse is true with the cyclopentane ring, because of an increased non-bonding interaction in the saturated five-membered ring. Therefore, conversion of cyclopentylidenemalononitrile into the corresponding cyclopropane would not be too highly favored. This view seems to gain a support from the observation that 2,5-dimethylcyclopentylidenemalononitrile did not produce the product at all apparently because of even greater interaction among the substituents in the five-membered ring of the product molecule.

Some large-membered cyclic ketones which had previously failed in the Wideqvist reaction (28) have now been found to produce 1,1,2,2-tetracyanocyclopropanes in good yield if they are first converted into the corresponding cycloalkylidenemalononitriles. A few 1,1,2,2-tetracyanocyclopropanes thus prepared are listed in Table 2. In a large-membered ring compound such as cyclopentadecylidenemalononitrile (XV), the methylene chain should be as free as if they were in an acyclic compound like 6-hendecylidenemalononitrile (XVI). This point makes it difficult to



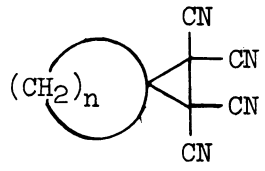

XV




XVI

explain why XVI fails to form the product, whereas XV yields the product.

Table 2. 1,1,2,2-Tetracyanocyclopropanes from Large-membered Cyclic Ketones



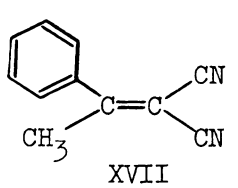

| n | Reaction time[a] | m.p., °C | Yield, % | NMR[b], $\tau$ |
|---|---|---|---|---|
| 9 | 15 mins. | 214-216 | 34.8 | 8.43 (s, 10.00 H)[d]<br>8.03 (m, 7.94 H) |
| 11 | 60 mins. | 197-200 | 94 | 8.53 (s, 14.00 H)[e]<br>8.09 (m, 8.02 H) |
| 14 | 6-7 days | 111-112 | 36[c] | 8.64 (s, 20.00 H)[d]<br>8.30 (m, 7.85 H) |

a. Time elapsed before the crystalline product appeared in the reaction mixture.
b. Inside the parentheses are described multiplicity of the peak and the number of hydrogens involved in that particular peak.
c. Yield based on the amount of the ketone.
d. NMR spectra run in DMSO-$d_6$ solutions.
e. NMR spectrum run in acetone-$d_6$.

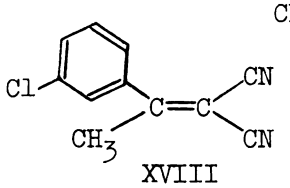
It is interesting to note that, in the NMR spectra of the three tetracyanocyclopropanes prepared from large-membered cyclic ketones (Table 2), eight hydrogens appear in a separate multiplet between $\tau$8.03 and $\tau$8.30. Incidentally, the eight hydrogens of 3,3-tetramethylene-1,1,2,2-tetracyanocyclopropane appeared in a peak at $\tau$7.91. This may be an indication that the eight hydrogens of the above three compounds come from those methylenes $\alpha$, $\beta$, $\alpha'$, $\beta'$ to the spiro carbon. However, it is possible that, due to the flexibility of the large ring, some methylenes other than those mentioned may be brought to the proximity of the cyano groups and are responsible for these multiplets of hydrogens. Perhaps, an experiment of deuterium substitution would give a more unequivocal answer to this problem.

B. Reaction of β-Arylalkylidenemalononitriles with Bromomalononitrile

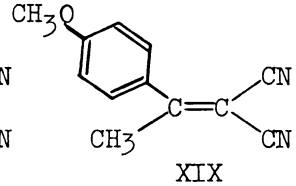
Table 3 lists a group of 3-alkyl-3-aryl-1,1,2,2-tetracyanocyclopropanes prepared from the corresponding β-arylalkylidenemalononitriles. β-Phenyl and β-m-chlorophenylethylidenemalononitrile (XVII and XVIII, respectively) reacted much faster than β-p-methoxyphenylethylidenemalononitrile (XIX). This may be explained by inductive and resonance effects. The phenyl and the m-chlorophenyl groups in XVII and XVIII,




XVII




XVIII

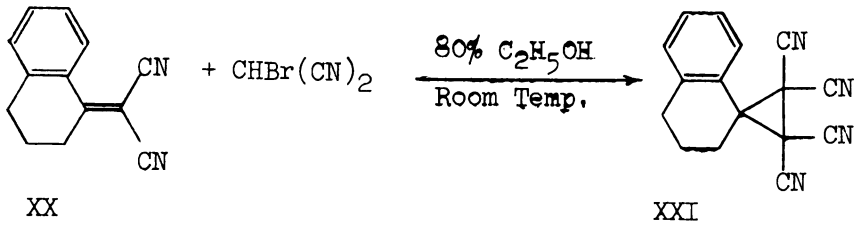



XIX

| | XVII | XVIII | XIX |
|---|---|---|---|
| t (hrs.) = | 1.5 | 2.0 | 20 |
| Yield (%) = | 86.6 | 68.1 | 51.2 |

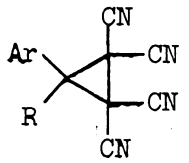
respectively, will undoubtedly exert an electron-withdrawing inductive effect. This will maintain the β-carbon of XVII and XVIII relatively positive, thus facilitating the attack of bromodicyanocarbanion. However, in the case of XIX, resonance through the p-methoxyphenyl group is likely to keep the β-carbon of XIX electron rich, thus retarding attack by the bromodicyanocarbanion.

With 2,3-benzocyclohexylidenemalononitrile (XX), the reaction seemed to take either of two courses, depending on the solvent and temperature. When 80% aqueous ethanol was used, at room temperature, the normal cyclopropanization reaction occurred.




XX XXI 13

Table 3. 3-Alkyl-3-aryl-1,1,2,2-tetracyanocyclopropanes



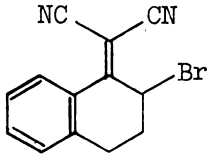

| R | Ar | Reaction time[a] | Yield, % |
|---|---|---|---|
| $CH_3$ | $C_6H_5$ | 90 mins. | 86.6 |
| $CH_3$ | m-$ClC_6H_4$ | 2 hrs. | 68.1 |
| $CH_3$ | p-$CH_3C_6H_4$ | 15 hrs. | 81.2 |
| $CH_3$ | p-$CH_3OC_6H_4$ | 20 hrs. | 51.2 |
| $CH_3$ | β-Naphthyl | 60 mins. | 54.8 |
| $C_2H_5$ | $C_6H_5$ | 2-3 days[b] | 17.8 |
| $CH_3$ | α-Thienyl | 30 mins. | 22.1 |
| 2,3-Benzocyclopentylidene | | 6-7 hrs. | 0 |
| 2,3-Benzocyclohexylidene | | 6-7 hrs. | 54.2 |

a. Time elapsed before the crystalline product separated in the reaction mixture.
b. This value is uncertain (see Experimental).

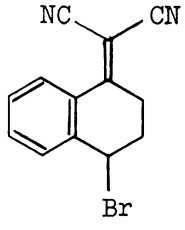
However, when the reaction was carried out at reflux or in 95% ethanol at room temperature, a pinkish bromine-containing compound, m.p. 135-138°, was obtained. Elemental analysis gave an empirical formula $C_{13}H_9BrN_2$.

The IR spectrum (in nujol) showed three absorption bands in the double bond region at 1603 $cm^{-1}$, 1567 $cm^{-1}$, and 1543 $cm^{-1}$, which are very similar in shape and relative intensity to that of the starting material XX (1599 $cm^{-1}$, 1564 $cm^{-1}$, and 1531 $cm^{-1}$). Also, the C≡N absorption band in the IR spectrum appeared at a much lower frequency (2245 $cm^{-1}$) than that of the tetracyanocyclopropane XXI indicating that the carbon-nitrogen triple bond is conjugated with an unsaturated system. The UV spectrum (in ethanol) showed two peaks, at 235 mμ (ε 6,830) and 322.5 mμ (ε 16,740), which again is similar to that of XX (229 mμ, ε 7,161; 233 mμ, ε 6,868; 311 mμ, ε 16,860). The absorption band at 233 mμ strongly suggests the presence of $\rangle C{=}C(CN)_2$ in the molecule, as the UV absorption of a number of alkylidenemalononitriles falls between 232 mμ, ε 11,920 (for isopropylidenemalononitrile) and 238 mμ, ε 12,918 (for 6-hendecylidene-malononitrile). Finally, the NMR spectrum (in DMSO-$d_6$) showed two multiplets at τ 7.55 and τ 6.94, a triplet at τ 4.36 ($J$ = 3.6 c.p.s.) and the aromatic multiplets at τ 2.47 and τ 1.73 in an area ratio of 1.97 : 2.01 : 0.92 : 4.00.

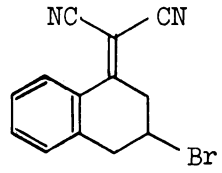
Possible structures for this compound are shown below (XXII-XXV).



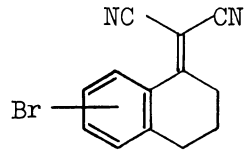

XXII




XXIII

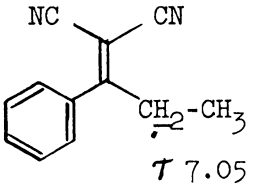



XXIV



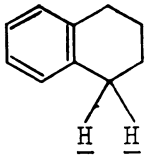

XXV

The structure XXV is eliminated because the aromatic multiplets in the NMR integrated as four hydrogens and also because the compound, on heating with pyridine for two minutes, readily loses the bromine, a phenomenon not usually expected from an aryl bromide. The debrominated compound, m.p. 158-159° dec., has not yet been completely identified. The structure XXIV agrees well with the analytical, IR, and UV data. However, it cannot comply with the NMR triplet at $\tau$4.36 and is eliminated on this ground. The structure of the brominated compound must, therefore, be either XXII or XXIII. Both structures retain the $\rangle C{=}C(CN)_2$ moiety and, in both compounds, the hydrogen attached to the brominated carbon should appear as a triplet in the NMR spectrum. Although no conclusive evidence is available, structure XXII appears to be more likely for the following reason. The NMR chemical shift (in $CDCl_3$) of the methylene hydrogens of $\beta$-phenylpropylidenemalononitrile (XXVI) occurs at $\tau$7.05 (31) and that of the $\alpha$-methylene hydrogens of tetralin (XXVII) at $\tau$7.24 (32). Imagine two brominated compounds XXVIII and XXIX. If Shoolery's effective shielding constant for the bromine (2.33 p.p.m.) is substracted from the methylene shifts of XXVI and XXVII, then the expected chemical shifts for the methine hydrogen of XXVIII and XXIX would be $\tau$4.72 and $\tau$4.91, respectively. Now, the methine shift of XXIII probably would not be much different from that of XXIX. However, the methine shift of XXII would be lower than that of XXVIII ($<\tau$4.72), because, in a rigid molecule like XXII, the methine hydrogen is likely to be held out of benzene plane. Thus the methine hydrogen of XXII is more likely to appear at as low field as $\tau$4.36 (observed).



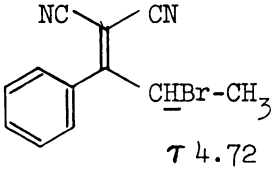

τ 7.05

XXVI



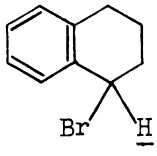

τ 7.24

XXVII



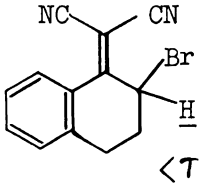

τ 4.72
(Expected)

XXVIII



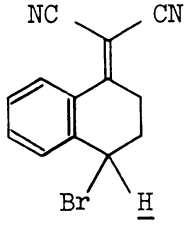

τ 4.91
(Expected)

XXIX




<τ 4.72
(Expected)

XXII




τ 4.91
(Expected)

XXIII

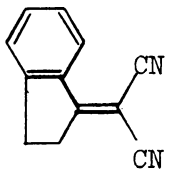
It is speculated that the bromination of XX may involve a free radical mechanism as shown in the Equation 14.

$$BrCH(CN)_2 \longrightarrow Br\cdot + \cdot CH(CN)_2 \qquad 14A$$

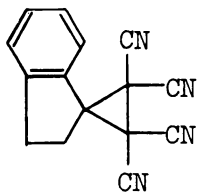
$$XX + \cdot CH(CN)_2 \longrightarrow XX\cdot + CH_2(CN)_2 \qquad 14B$$

$$XX\cdot + BrCH(CN)_2 \longrightarrow XX\text{-}Br + \cdot CH(CN)_2 \qquad 14C$$

A similar type of bromination was observed in the reaction of 2,3-benzocyclopentylidenemalononitrile (XXX) and bromomalononitrile. The desired product (XXXI) was not obtained. Instead, there were obtained off-white



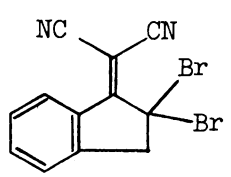

XXX

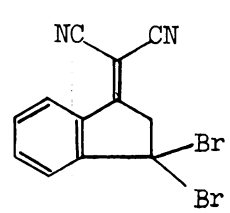


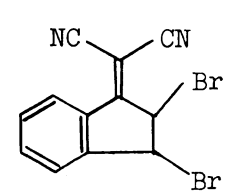

XXXI

crystals, m.p. 208-211°, which, on standing, became magenta. Analysis gave an empirical formula $C_{12}H_5Br_2N_2$, which is an impossible formula, but could very well be considered to be $C_{12}H_6Br_2N_2$. The IR spectrum (in nujol) showed a C≡N absorption band at as low frequency as XXX (2240 $cm^{-1}$), indicating a conjugated cyano group. Furthermore, two IR absorption bands at the double bond region, 1599 $cm^{-1}$ and 1568 $cm^{-1}$, were similar in shape and in relative intensity to those of XXX (1601 $cm^{-1}$ and 1568 $cm^{-1}$).

The UV spectrum (in ethanol) showed a peak at 236 mμ (ε7,140) and two ill-defined peaks at 337 mμ (ε15,859) and 346 mμ (ε15,731). These data are favorably compared to 234 mμ (ε8,170), 306 mμ (ε17,480), and 333 mμ (ε19,722) of the starting material XXX*. Again, the peak at 236 mμ (ε7,140) is indicative of the presence of $\rangle C{=}C(CN)_2$ moiety in the molecule. Unfortunately, it was not possible to find a suitable solvent to determine the NMR spectrum. Possible structures for this compound are shown below.



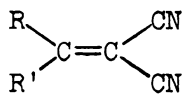




cis and trans

* The UV spectrum of 2,3-benzocyclopentylidenemalononitrile (XXX) showed an additional two peaks at 206 mμ (ε7,229) and 211 mμ (ε6,258).

The following substituted 1,1-dicyanoethylenes did not give any isolable products on reaction with bromomalononitrile.



XXXII

XXXIIa R = R' = $C_6H_5$
XXXIIb R = H; R' = $C_2H_5O$
XXXIIc R = $CH_3$; R' = $C_2H_5O$
XXXIId R, R' = Ethylenedioxy
XXXIIe R = R' = CN

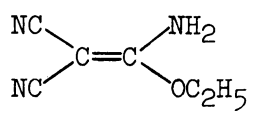
The failure of diphenylmethylenemalononitrile (XXXIIa) might be caused by the steric effect of the two phenyl groups. The failure of β-alkoxyl derivatives (XXXIIb-d) might be ascribed to the resonance effect of alkoxyl group, which would keep the β-carbon rich in electrons. It is not possible to present a plausible reason why tetracyanoethylene (XXXIIe) failed to produce the product.

When an excess of bromomalononitrile was allowed to react with an alkylidenemalononitrile, especially for a prolonged time, there was usually obtained, in addition to the desired tetracyanocyclopropane, a small amount of crystals, which did not melt sharply but sublimed at 270-300°. The substance contained bromine and nitrogen. The IR spectrum (both in nujol and KBr pellet) did not show any significant absorption bands. The NMR spectrum (in $D_2O$) showed a singlet at $\tau$5.15. This substance was identified as ammonium bromide.

When excess bromomalononitrile was allowed to react with 3,3-dimethyl-2-butylidenemalononitrile in aqueous ethanol (about 85%) for a prolonged time (a week to a month), no cyclopropane was produced. Instead, there was

obtained a brown precipitate which, on treating with Norit A, became white crystals. This compound was also obtained by similarly treating bromomalononitrile with other alkylidenemalononitriles which failed to yield tetracyanocyclopropanes; for example, 2,4-dimethyl-3-pentylidenemalononitrile, 6-hendecylidenemalononitrile, tetracyanoethylene, etc. The fact that different alkylidenemalononitriles produced the same compound suggested that the formation of this compound did not involve the alkylidenemalononitrile. Indeed, when an aqueous ethanol solution of bromomalononitrile was refluxed for several hours, this compound, as well as ammonium bromide, was obtained. The analysis of the sample, m.p. 235-237° gave an empirical formula $C_6H_7N_3O$. The IR spectrum (in nujol) showed the absorption bands at 3355 $cm^{-1}$, 3230 $cm^{-1}$ (both for NH), 2248 $cm^{-1}$, 2205 $cm^{-1}$ (both for CN), 1658 $cm^{-1}$, 1550 $cm^{-1}$, 1503 $cm^{-1}$ (C=C and/or NH), 1043 $cm^{-1}$ (C-O-C), and many other minor bands. The UV spectrum (in ethanol) gave a single absorption band at 253 mμ (ε 18,636). Finally, the NMR spectrum (in DMSO-d6) showed a triplet and a quartet (J = 7.0 c.p.s. for both peaks) at τ8.71 and τ5.72, respectively, (strongly indicative of an ethoxyl group) and a singlet at τ1.45 in an area ratio of 3.00 : 1.98 : 1.98.

The analytical and spectral data suggest that the possible structures are XXXIII and XXXIIIa.



XXXIII

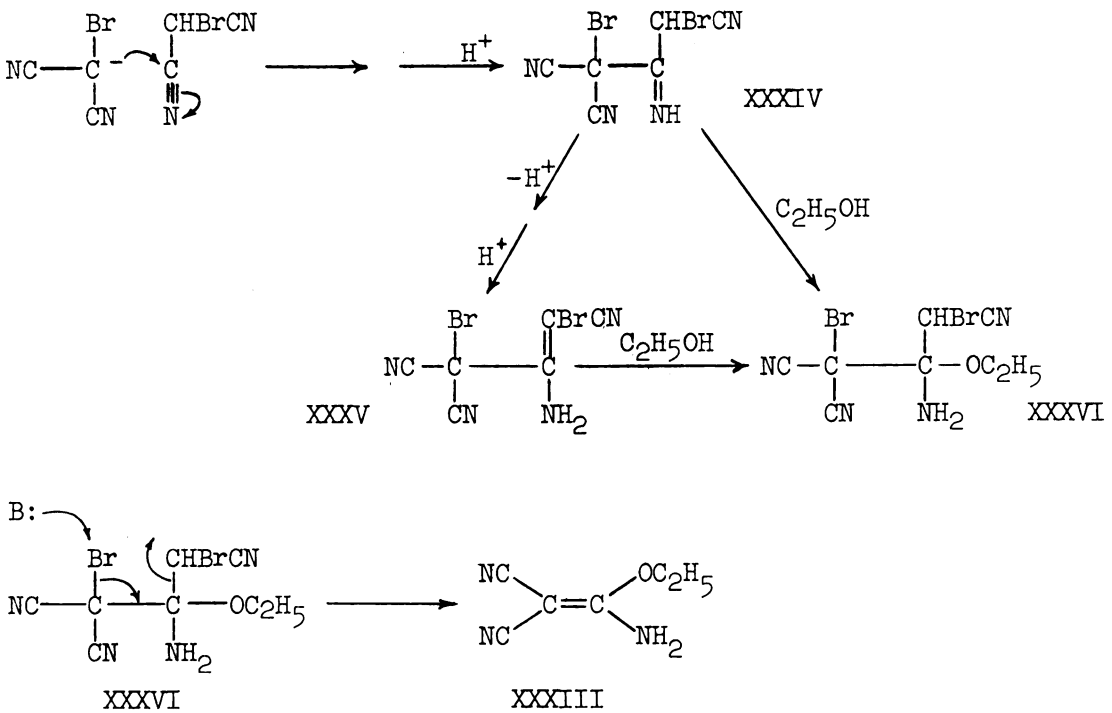
$NC-C(NH_2)=C(OC_2H_5)-CN$

XXXIIIa

However, XXXIIIa was eliminated because the compound appears to be identical with XXXIII previously reported in the literature (33), m.p. 225-226° (IR: 3.05 μ, 3.19 μ, 6.05 μ, 6.48 μ; UV: 254 mμ).

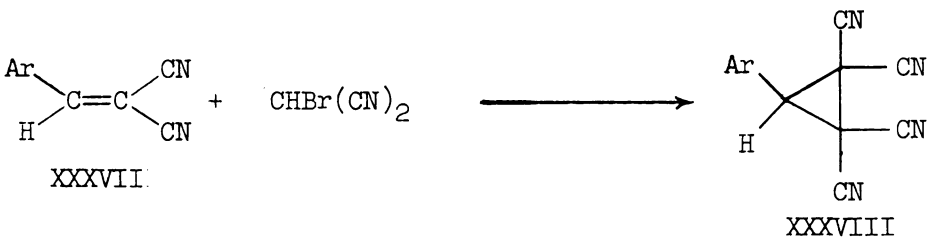
A possible mechanism for the formation of XXXIII is proposed in Scheme 1.

Scheme 1




Bromodicyanocarbanion attacks on the cyano carbon of bromomalononitrile to give the imino compound XXXIV. XXXIV tautomerized to XXXV which adds ethanol across the double bond to give XXXVI. Or XXXVI can be formed by direct addition of ethanol to the imino double bond of XXXIV. The exact nature of the products from the final elimination step is not known. Possible candidates for the nucleophile are bromide ion, or bromodicyanocarbanion. Bromoacetonitrile or its hydrolysis product may also be formed. A few possible precedents for the last step of the elimination have been encountered and are described on pages 47, 50, and 60, respectively.

C. Reaction of Arylidenemalononitriles with Bromomalononitrile*




XXXVII XXXVIII

15

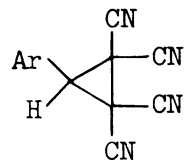
Table 4 lists the 3-aryl-1,1,2,2-tetracyanocyclopropanes (XXXVIII) prepared according to Equation 15, together with some of the pertinent data. In most cases, an arylidenemalononitrile (XXXVII) seems to react with bromomalonitrile to form the product much faster than an alkylidenemalononitrile having an equal number of carbons. This may be due to the fact that the electron-withdrawing nature of the phenyl makes the β-carbon of XXXVII positive. It may also be ascribed to the steric effect, i.e., the arylidenemalononitriles have only one substituent at the β-carbon, whereas the alkylidenemalononitriles described earlier bear two β-substituents.

When Ar of XXXVII was a phenyl or a phenyl with an electron-withdrawing substituent, the time required for the formation of product was just a few minutes. However, there were a few exceptions. For example, m-chlorobenzylidenemalononitrile (XXXIX) and o-nitrobenzylidenemalononitrile (XL) required 30 minutes and 2,6-dichlorobenzylidenemalononitrile (XLI) an hour The longer time required by XL and XLI may be explained by the steric effect exerted by a nitro group or by two chlorine atoms in the ortho positions.

---

* Arbitrarily included with arylidenemalononitriles are those benzylidenemalononitriles, with or without substituents, that retain the β-hydrogen.

Table 4. 3-Aryl-1,1,2,2-tetracyanocyclopropanes




| Ar. | Reaction Time[a] | M.P.(dec.), °C | Yield, % | Analysis[b] C | H | N | X |
|---|---|---|---|---|---|---|---|
| $C_6H_5$ [c] | A few mins. | 227-230 | 91.7 | - | - | - | - |
| o-$ClC_6H_4$ | A few mins. | 246-248 | 98 | 61.87 (61.80) | 2.21 (2.00) | 22.20 (22.18) | 14.21 (14.03) |
| m-$ClC_6H_4$ | 30 mins. | 183-185 [d] | 82 | 61.85 (61.80) | 2.16 (2.00) | 22.16 (22.18) | 14.20 (14.03) |
| p-$ClC_6H_4$ [e] | A few mins. | 248-250 | 85.5 | - | - | - | - |
| o-$O_2NC_6H_4$ | 30 mins. | 211-213 | 95.8 | 59.40 (59.32) | 1.71 (1.92) | 26.59 (26.61) | - |
| m-$O_2NC_6H_4$ [f] | A few mins. | 246-248 | 73.7 | - | - | - | - |
| p-$O_2NC_6H_4$ | A few mins. | 232-235 | 94 | 59.38 (59.32) | 2.12 (1.91) | 26.50 (26.61) | - |
| o-$BrC_6H_4$ | A few mins. | 249-252 | 87.5 | 52.74 (52.55) | 1.85 (1.70) | 18.85 (18.86) | 26.92 (26.90) |
| p-$NCC_6H_4$ | A few mins. | 264 | 97.4 | 68.89 (69.13) | 2.27 (2.07) | 28.24 (28.80) | - |
| p-$CH_3C_6H_4$ | 20 mins. | 227-230 | 90.5 | 72.46 (72.40) | 3.46 (3.47) | 24.22 (24.13) | - |

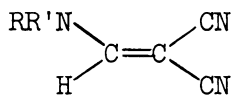
Table 4. Continued

| Ar | Reaction Time[a] | M.P.(dec.),°C | Yield,% | Analysis[b] C | H | N | X |
|---|---|---|---|---|---|---|---|
| p-$CH_3OC_6H_4$ | A few hrs. | 209-210 | 75 | 67.62 (67.74) | 3.26 (3.25) | 22.40 (22.57) | - |
| 2,4-$Cl_2C_6H_3$ [g] | 9 days | 225-228 [h] | 93.2 | 54.46 (54.38) | 1.50 (1.40) | 19.45 (19.52) | 24.60 (24.70) |
| 2,6-$Cl_2C_6H_3$ | 1 hr. | 227-230 | 91.6 | 54.59 (54.38) | 1.46 (1.40) | 19.54 (19.52) | 24.65 (24.70) |
| 3,4-$CH_2O_2C_6H_3$ [i] | 24 hrs. | 222-223 | 68 | 64.18 (64.12) | 2.50 (2.31) | 21.20 (21.37) | - |
| 1-Naphthyl | Within 1 min. | 249-252 | 99 | 76.21 (76.11) | 3.06 (3.01) | 20.82 (20.89) | - |
| 2-Naphthyl | A few mins. | 236-240 | 99 | - | - | - | - |
| 2-Furyl [j] | 10 mins. | 203-208 | 48.5 | - | - | - | - |

a. Time elapsed before product began to separate in the reaction mixture. b. Figures in parentheses are the calculated values and X denotes halogen. c. Lit. val. (3) m.p. 221° dec. d. Melted without decomposition. e. Lit. val. (4) m.p. 240-241° dec. f. Lit. val. (4) m.p. 245-246° dec. g. 2,4-dichlorobenzylidene-malononitrile (1g., 4.48 mmoles) and bromomalononitrile (0.95 g., 6 mmoles) were dissolved in 80 ml. of an ethanol-THF mixture. The solution was kept at room temperature for 9 days. Product was obtained after removal of the solvent followed by recrystallization from ethanol. h. Melted without decomposition. i. Piperonylidenemalononitrile (1 g., 5.05 mmoles) and bromomalononitrile (1.09 g., 7.50 mmoles) were dissolved in 300 ml. of ethanol and kept at room temperature for 24 hrs. Precipitate that has formed on adding 100 ml. of water to the reaction mixture was recrystallized from ethanol. j. Lit. val. (3) m.p. 190-200 ° dec. It has been found that this compound could also be prepared in the following manner: Furfural (1 g., 6.9 mmoles) and bromomalononitrile (1 g., 6.9 mmoles) were dissolved in 10 ml. of 50% aqueous ethanol and the mixture was kept for 5 hrs. in a dark place at room temperature. The crystals that had formed were filtered and recrystallized from an ethanol-acetone mixture, m.p. 209-212 ° dec., 0.3 g. (41.8%).

If, however, Ar of XXXVII is a phenyl with an electron-releasing substituent, then product formation requires a longer time presumably because of the resonance effect caused by the substituent. This observation seems to suggest that an electron-withdrawing substituent may not always facilitate the reaction, but an electron-releasing substituent does slow the reaction down.

The NMR spectra of arylidenemalononitriles showed the vinyl hydrogen between $\tau$ 1.13 (p-nitrobenzylidenemalononitrile) and $\tau$ 1.90 (p-methoxybenzylidenemalononitrile). The vinyl hydrogen of 1-naphthalmalononitrile appeared at unusually low field ($\tau$ 0.60). The vinyl hydrogen of an N-substituted 1-amino-2,2-dicyanoethylene (XLII), which bears some relationship to an arylidenemalononitrile, was reported to range between $\tau$ 2.20 (R = $CH_3$, R' = H) and $\tau$ 2.92 (R, R' = pentamethylene) (34).

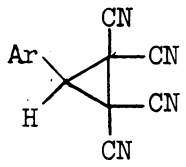


XLII

When an arylidenemalononitrile (XXXVII) is converted to a 3-aryl-1,1,2,2-tetracyanocyclopropane (XXXIII), the vinyl hydrogen becomes the cyclopropyl hydrogen, appearing between $\tau$ 4.51 (XXXVIII, Ar = o-$O_2NC_6H_4$) and $\tau$ 5.27 (XXXVIII, Ar = p-$CH_3OC_6H_4$). A remarkably low chemical shift for the cyclopropyl hydrogen of XXXVIII has been ascribed to the fact, that, in XXXVIII, the cyano groups are oriented in such a position that the anisotropy of carbon-nitrogen triple bond deshields the cyclopropyl hydrogen (4).

In the NMR spectra of 3-aryl-1,1,2,2-tetracyanocyclopropanes XXXVIII, the cyclopropyl hydrogen was shown to couple with the ortho hydrogens of

Table 5. Some NMR Spectral Data of 3-Aryl-1,1,2,2-tetracyanocyclopropanes[a]

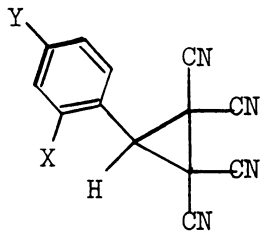



| Ar. | H, Cyclopropyl[b] | H, Aromatic | | |
|---|---|---|---|---|
| $C_6H_5$ | 5.13(t, 0.8) | 2.56(m) | 2.26(m) | |
| o-$ClC_6H_4$ | 5.03(d, 1.0) | 2.30(m) | 1.92(m) | |
| m-$ClC_6H_4$ | 5.07(t, 1.0)[c] | 2.50(m) | 2.31(m) | 2.07(m) |
| p-$ClC_6H_4$ | 5.06(t, 0.9) | 2.46(d) | 2.14(d) | ($A_2B_2$) |
| o-$O_2NC_6H_4$ | 4.51(d, 0.9)[d] | 2.02(m) | 1.65(m) | |
| m-$O_2NC_6H_4$ | 4.85(q, 0.9) | 2.22(s)<br>1.56(m) | 2.07(s)<br>1.04(m) | 1.94(s) |
| p-$O_2NC_6H_4$ | 4.94(t, 0.8) | 1.93(d) | 1.67(d) | ($A_2B_2$) |
| p-$NCC_6H_4$[e] | 4.77(t, 0.6) | 1.93(d) | 1.73(d) | ($A_2B_2$) |
| o-$BrC_6H_4$ | 5.14(d, 0.9) | 2.58(m) | 2.27(m) | |
| p-$CH_3C_6H_4$[f] | 5.16 | 2.64(d) | 2.27(d) | ($A_2B_2$) |
| p-$CH_3OC_6H_4$ | 5.27 | 2.95(d) | 2.27(d) | ($A_2B_2$) |
| 2,4-$Cl_2C_6H_3$ | 5.02(d, 1.0) | 2.13(m) | | |
| 2,6-$Cl_2C_6H_3$ | 4.94 | 2.26(s) | | |
| 3,4-$CH_2O_2C_6H_4$ | 5.23(t, 0.95) | 3.17(s) | 3.02(s) | 2.73(m) |
| 1-Naphthyl | 4.56 | 2.11(m) | 1.85(m) | |
| 2-Naphthyl | 4.84 | 2.34(m) | 2.00(m) | 1.50(s) |
| 2-Furyl | 4.60 | 3.41(q) | 3.07(m) | 2.17(m) |

a. Unless otherwise stated, the spectra were taken in an acetone solution and the chemical shifts were expressed in $\tau$ units. b. In the parentheses, small letter designate the multiplicity of the peak and the figure the coupling constant (J) in c.p.s. c. Central peak of this triplet was further split into a triplet, J = 0.4 c.p.s. d. This peak appears to consist of 2 doublets each with J = 0.9 c.p.s. e. The NMR spectrum was run in dimethyl sulfoxide solution. The values in acetone solution are $\tau$4.52 for H, cyclopropyl and $\tau$1.98(d) and $\tau$1.81(d) in an $A_2B_2$ pattern for H, aromatic. f. The NMR spectrum was run in acetone-d6 solution.

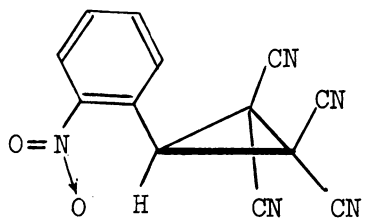
the aromatic ring with a coupling constant between 0.6 c.p.s. (XXXVIII, Ar = p-$NCC_6H_4$) and 1.0 c.p.s. (XXXVIII, Ar = o-$ClC_6H_4$). In Table 5 are listed the data of chemical shift, multiplicity, and coupling constant of the cyclopropyl hydrogens.

3-Aryl-1,1,2,2-tetracyanocyclopropanes in which one of two ortho hydrogens was substituted gave a doublets for the cyclopropyl hydrogens. This would be expected if the cyclopropyl hydrogen is coupled to one ortho hydrogen.

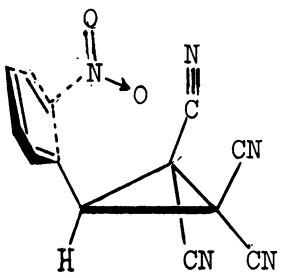



| | | |
|---|---|---|
| X = Cl, Y = H (d, J = 1.0 c.p.s.) | | Fig. 1 |
| X = Br, Y = H (d, J = 0.9 c.p.s.) | | Fig. 2 |
| X = Cl, Y = Cl (d, J = 1.0 c.p.s.) | | Fig. 3 |
| X = $NO_2$, Y = H (2 doublets J = 1.0 c.p.s. for both) | | Fig. 4 |

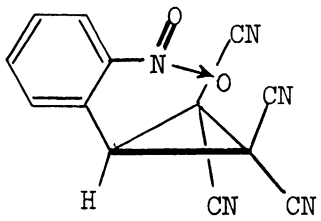
However, 3-o-nitrophenyl-1,1,2,2-tetracyanocyclopropane showed two doublets for the cyclopropyl hydrogen. Three different conformations are shown below, i.e. XLIIIa, XLIIIb, and XLIIIc.



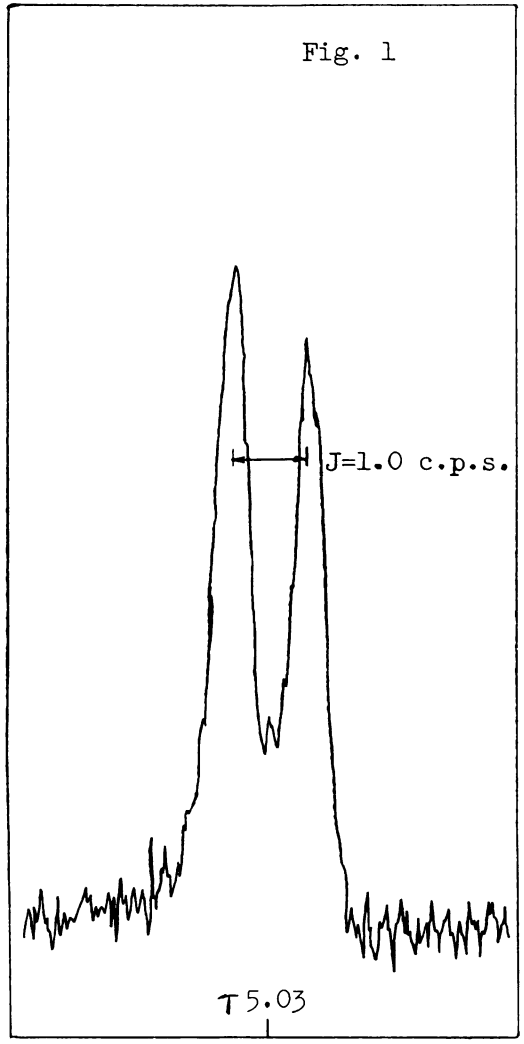

XLIIIa

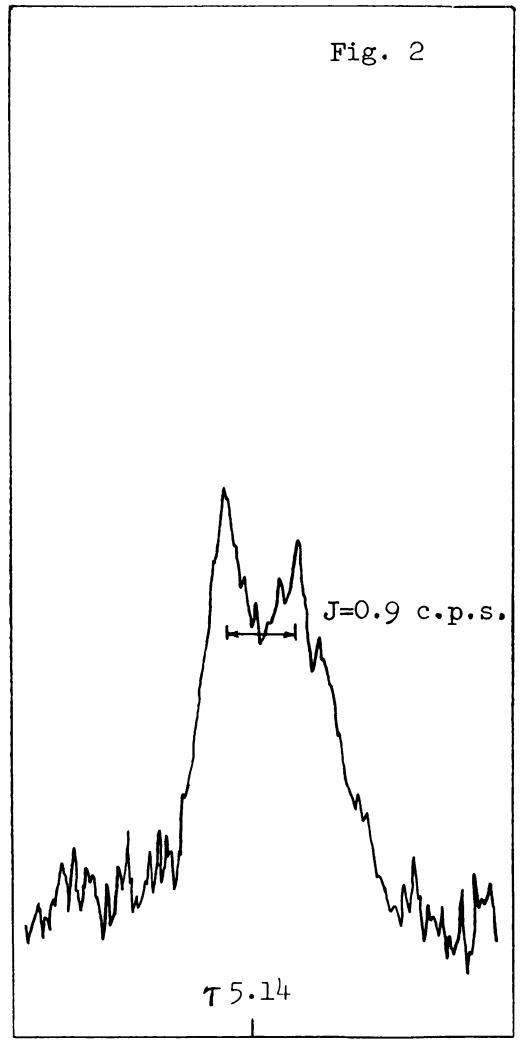



XLIIIb




XLIIIc



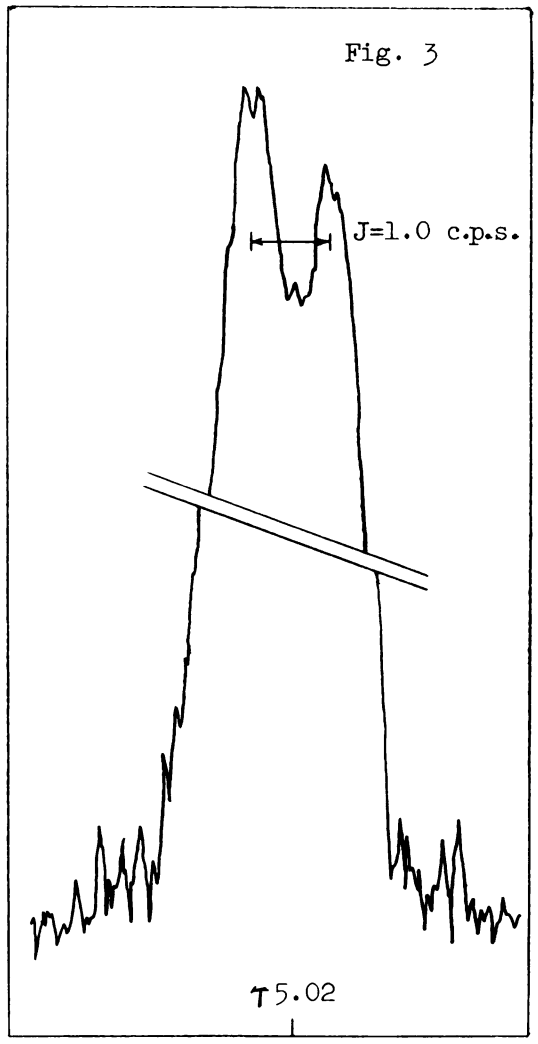
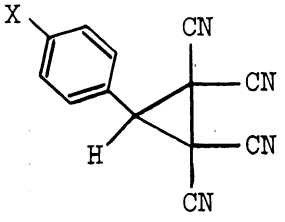




Fig. 1. NMR Spectrum of Cyclopropyl Hydrogen of 3-o-Chlorophenyl-1,1,2,2-tetracyanocyclopropane.
Fig. 2. NMR Spectrum of Cyclopropyl Hydrogen of 3-o-Bromophenyl-1,1,2,2-tetracyanocyclopropane.
Fig. 3. NMR Spectrum of Cyclopropyl Hydrogen of 3-(2',4'-Dichlorophenyl)-1,1,2,2-tetracyanocyclopropane.

An equilibrium between any two conformers could result in two doublets. However, XLIIIc seems very unlikely because of steric reason. XLIIIb would be sterically most favored (35). XLIIIa, although sterically less favored than XLIIIb, may be electronically more favored; that is, in XLIIIa, the $\pi$-electrons of the phenyl ring could overlap with those of the cyclopropane ring and possibly with the two cyano groups. Therefore, 3-o-nitrophenyl-1,1,2,2-tetracyanocyclopropane may be in equilibrium between the two conformers, XLIIIa and XLIIIb. This may possibly give rise to two doublets for the cyclopropyl hydrogen. Or the cyclopropyl hydrogen may be split by the ortho hydrogen and the para hydrogen. No unambiguous conclusion could be drawn from the data obtained.

3-Phenyl-1,1,2,2-tetracyanocyclopropane and 3-aryl-1,1,2,2-tetracyanocyclopropanes having a substituent at the para position gave a triplet for the cyclopropyl hydrogens. This is expected because, with free rotation along the phenyl-cyclopropyl bond, there would be two equivalent ortho hydrogens. 3-p-Methylphenyl-1,1,2,2-tetracyanocyclopropane and 3-p-methoxyphenyl-1,1,2,2-tetracyanocyclopropane did not give a resolved triplet, but the peaks were shaped like a triplet.




| | |
|---|---|
| X = H (t, J = 0.8 c.p.s.) | Fig. 5 |
| X = Cl (t, J = 0.9 c.p.s.) | Fig. 6 |
| X = $NO_2$ (t, J = 0.8 c.p.s.) | Fig. 7 |
| X = CN (t, J = 0.6 c.p.s.) | Fig. 8 |

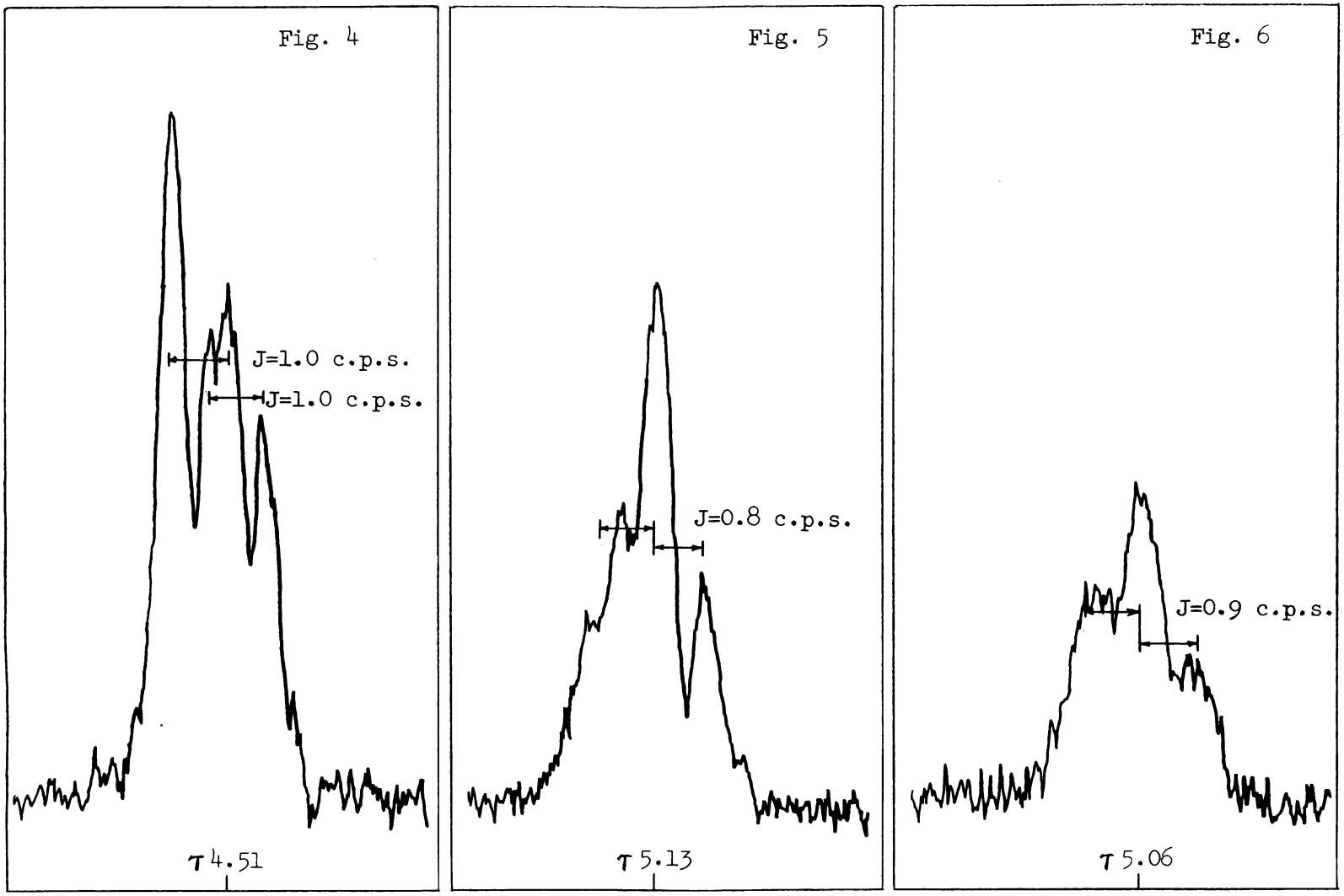
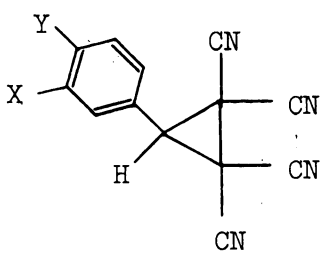



Fig. 4. NMR Spectrum of Cyclopropyl Hydrogen of 3-o-Nitrophenyl-1,1,2,2-tetracyanocyclopropane.
Fig. 5. NMR Spectrum of Cyclopropyl Hydrogen of 3-Phenyl-1,1,2,2-tetracyanocyclopropane.
Fig. 6. NMR Spectrum of Cyclopropyl Hydrogen of 3-p-Chlorophenyl-1,1,2,2-tetracyanocyclopropane.

In 3-aryl-1,1,2,2-tetracyanocyclopropanes with a meta substituent, the two ortho hydrogens are no longer equivalent. Therefore there should be two doublets for the cyclopropyl hydrogen. This was the case with 3-m-nitrophenyl-1,1,2,2-tetracyanocyclopropane, which showed two doublets. 3-(3',4'-Methylenedioxyphenyl)-1,1,2,2-tetracyanocyclopropane showed a triplet. This may be so probably because the original two doublets might have been so placed as to make a triplet. 3-m-chlorophenyl-1,1,2,2-tetracyclopropane showed a complicated spectrum (Fig. 11), that is, the




| | | |
|---|---|---|
| $X = NO_2$, $Y = H$ | (2 doublets $J = 0.8$ c.p.s. for both) | Fig. 9 |
| X, Y = $-OCH_2O-$ | (t, $J = 0.95$ c.p.s.) | Fig. 10 |

spectrum seemed to be a triplet, J = 1.0 c.p.s.,with the central peak further split into a smaller triplet, J = 0.4 c.p.s. A satisfactory explanation for the complexity of this spectrum cannot be offered at this time.

More convincing evidence for four bond coupling between the cyclopropyl hydrogen ($H_4$) and the aromatic ortho hydrogen ($H_1$) of a 3-aryl-1,1,2,2-tetracyanocyclopropane was obtained from the observation that, in 3-(2',4'-dichlorophenyl)-1,1,2,2-tetracyanocyclopropane (XLIV), indeed $H_1$ and $H_4$ were shown to couple to each other, J = 1.0 c.p.s. (Fig. 14). The other coupling constants observed were J ($H_1$, $H_2$) = 8.35 c.p.s., J ($H_2$, $H_3$) =

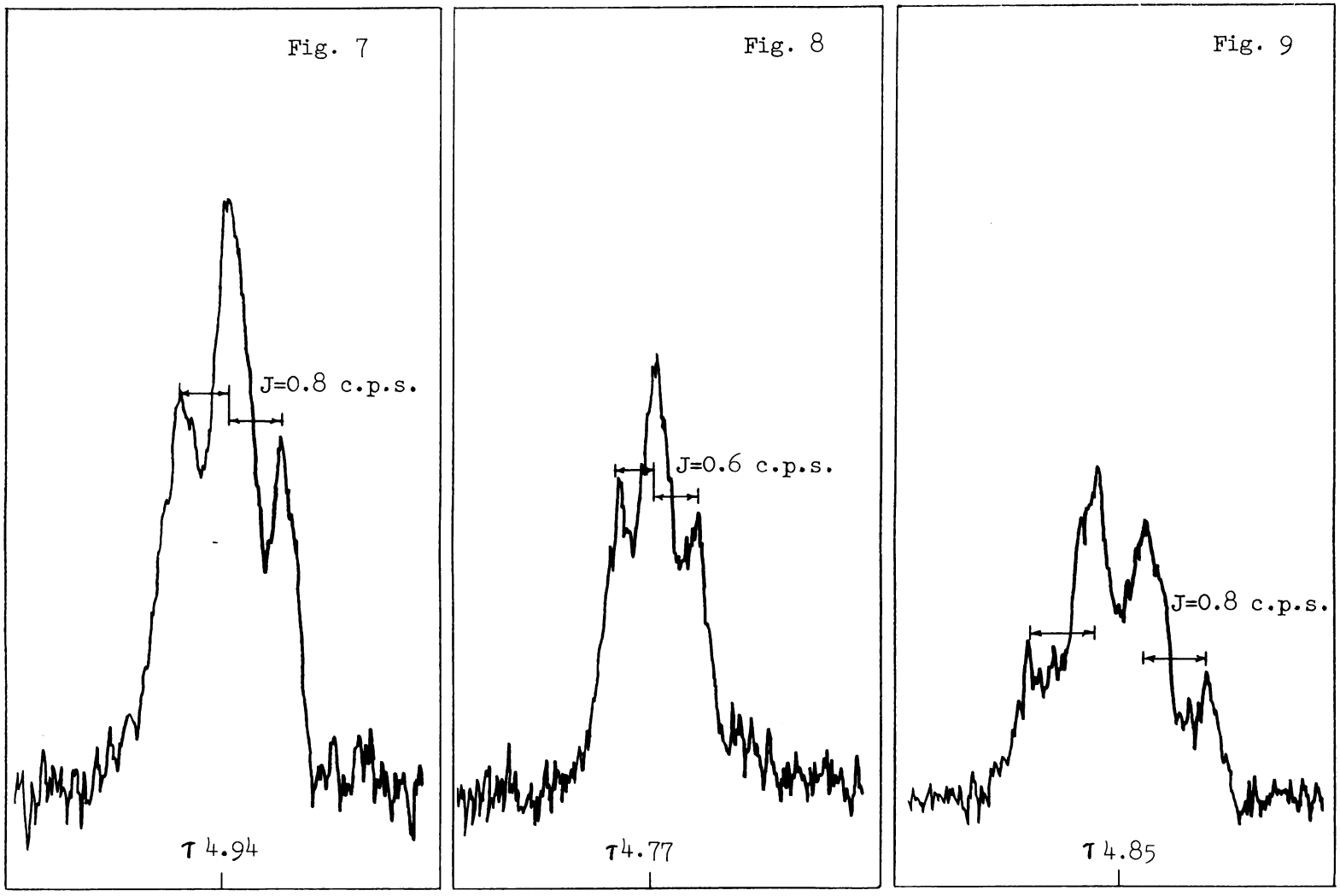
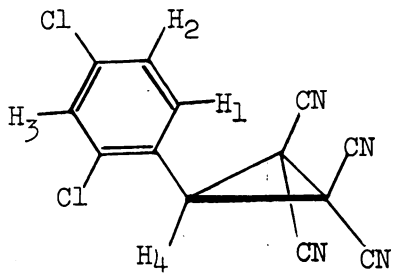


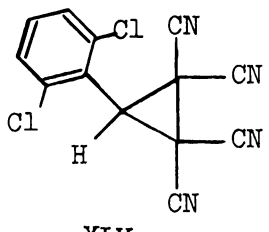

Fig. 7. NMR Spectrum of Cyclopropyl Hydrogen of 3-p-Nitrophenyl-1,1,2,2-tetracyanocyclopropane.
Fig. 8. NMR Spectrum of Cyclopropyl Hydrogen of 3-p-Cyanophenyl-1,1,2,2-tetracyanocyclopropane (in DMSO).
Fig. 9. NMR Spectrum of Cyclopropyl Hydrogen of 3-m-Nitrophenyl-1,1,2,2-tetracyanocyclopropane.




XLIV

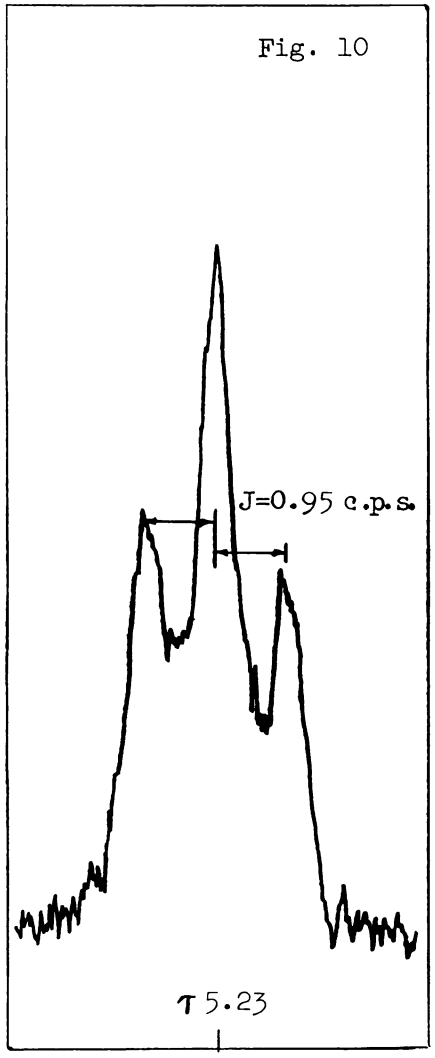
2.05 c.p.s., and $J(H_1, H_3)$ = 0.45 c.p.s. The $H_1$ appeared at the lowest field. This may be explained as follows. Due to restricted rotation of the bond between the cyclopropyl and phenyl groups, XLIV would be likely to retain the conformation shown above. Consequently, $H_1$ is the aromatic hydrogen brought closest to the cyano groups and is least shielded. This would be probably true of most 3-aryl-1,1,2,2-tetracyanocyclopropanes having an ortho substituent.

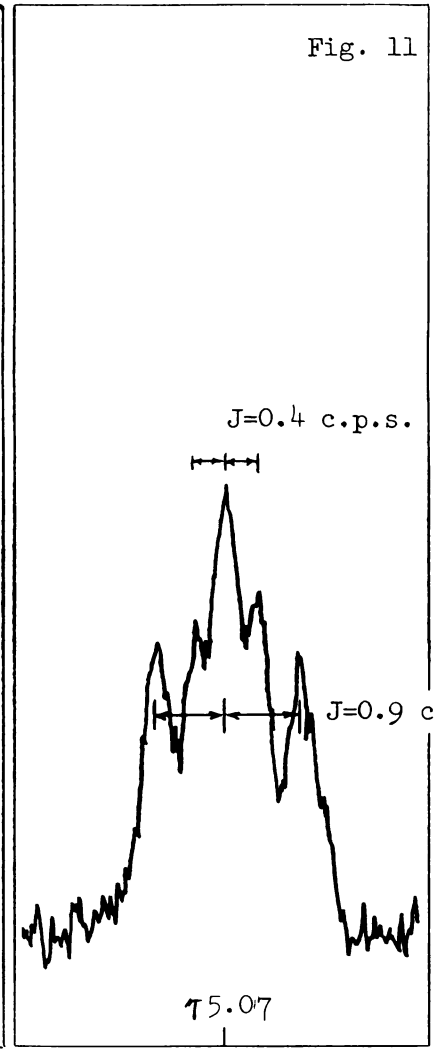
If only the ortho hydrogens are involved in coupling with the cyclopropyl hydrogen, 3-(2',6'-dichlorophenyl)-1,1,2,2-tetracyanocyclopropane (XLV) where both ortho hydrogens are replaced by chlorine should give an unsplit singlet for the cyclopropyl hydrogen. This is the case with a DMSO solution of XLV (Fig. 12). However, an acetone solution of XLV gave,

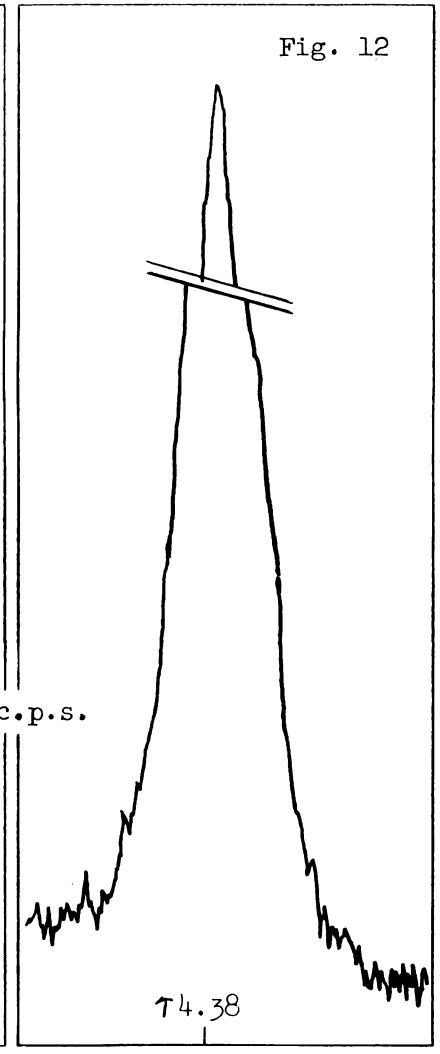



XLV

in addition to the main peak, a small shoulder (Fig. 13). What caused this shoulder cannot be answered at this time.



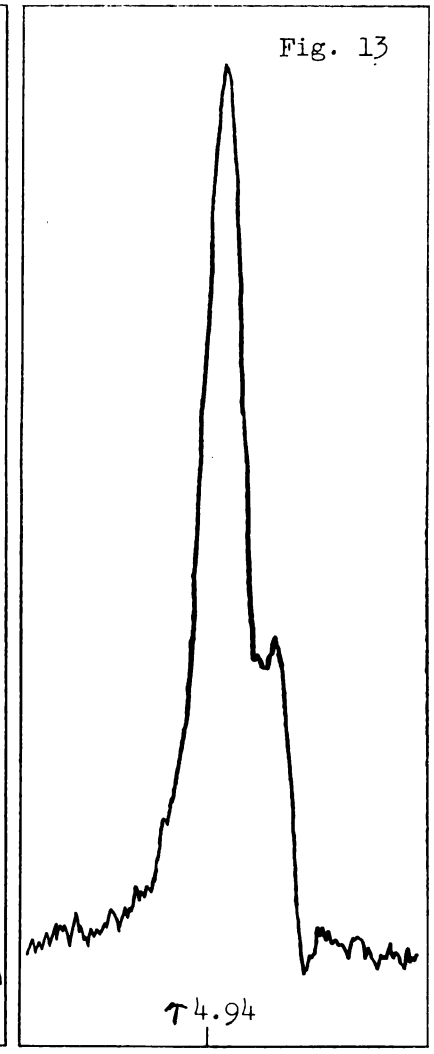




Fig. 10. NMR Spectrum of Cyclopropyl Hydrogen of 3-(3',4'-Methylenedioxyphenyl)-1,1,2,2-tetracyanocyclopropane.

Fig. 11. NMR Spectrum of Cyclopropyl Hydrogen of 3-m-Chlorophenyl-1,1,2,2-tetracyanocyclopropane.

Fig. 12. NMR Spectrum of Cyclopropyl Hydrogen of 3-(2',6'-Dichlorophenyl)-1,1,2,2-tetracyanocyclopropane (in DMSO).

Fig. 13. NMR Spectrum of Cyclopropyl Hydrogen of 3-(2',6'-Dichlorophenyl)-1,1,2,2-tetracyanocyclopropane (in acetone).

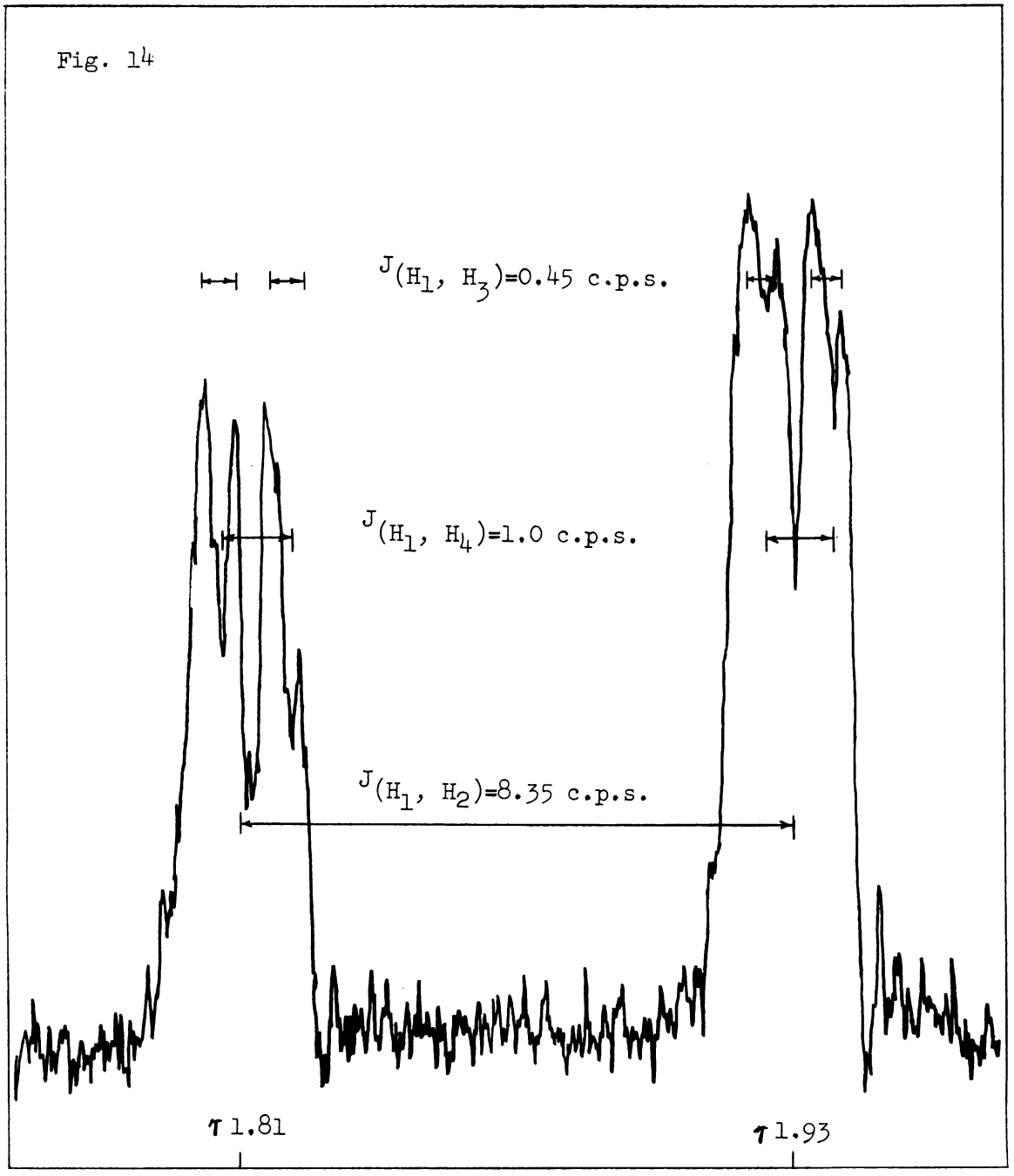
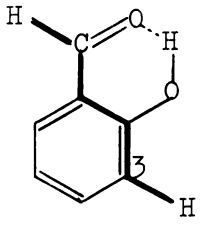
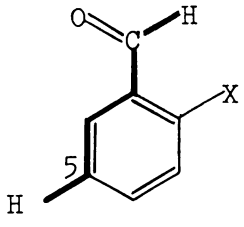



Fig. 14. NMR Spectrum of <u>ortho</u>-Hydrogen of 3-(2',4'-Dichlorophenyl)-1,1,2,2-tetracyanocyclopropane.

Long range coupling between an aromatic hydrogen and a hydrogen of the $sp^2$ carbon directly attached to that aromatic ring seems to require the hydrogens participating in the coupling to be on a "zig-zag path" (or trans-trans path) such as shown by the heavy lines in XLVI and XLVII. For example, in salicylaldehyde where the hydroxyl group is hydrogen-bonded to the carbonyl oxygen (XLVI), the aldehydic hydrogen couples only with the meta hydrogen at the $C_3$-position. However, in other ortho sub-



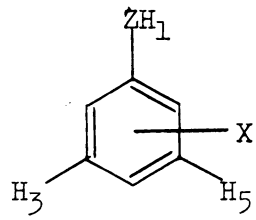

XLVI




XLVII

stituted benzaldehydes where no intramolecular hydrogen bonding is possible and the carbonyl oxygen, because of steric reasons, is sided with the unsubstituted part of the benzene ring (XLVII), the aldehydic hydrogen couples only with the meta hydrogen at the $C_5$ position (36).

Recently, long range coupling of the system represented by formula XLVIII, where Z is an $sp^2$ hybridized carbon, nitrogen, or oxygen, has been extensively investigated (37). With some exceptions, the data generally confirms the trans-trans coupling. To quote a few examples, salicylaldehyde (XLVIII, Z = CO, X = 2-OH) showed $H_1$ as a doublet (in $CH_2Br_2$) with J ($H_1$, $H_3$) = 0.6 c.p.s. and J ($H_1$, $H_5$) = 0 c.p.s. In o-chlorobenzaldehyde (XLVIII, Z = CO, X = 2-Cl), $H_1$ was a doublet (in $CH_2Br_2$ and DMSO) with J = ($H_1$, $H_5$) = 0.7 c.p.s. and J ($H_1$, $H_3$) = 0 c.p.s. A triplet (in acetone)




XLVIII

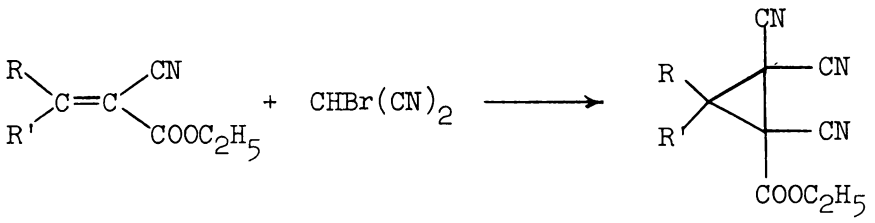
was observed for $H_1$ of p-nitrobenzaldehyde (XLVIII, Z = CO, X = 4-$NO_2$), J = 0.35 c.p.s. It is so because, due to free rotation of the bond joining the formyl group and phenyl group, $H_1$ can be trans-trans oriented to both $H_3$ and $H_5$, thus split by these two equivalent hydrogens.

By analogy with the trans-trans coupling between the aromatic hydrogens and the hydrogen of the $sp^2$ carbon mentioned above, the cyclopropyl hydrogen of 3-aryl-1,1,2,2-tetracyanocyclopropanes, because of some $sp^2$ character of the cyclopropyl ring carbon (38), might be expected to couple with the meta hydrogens, which can truly be trans-trans oriented with respect to the cyclopropyl hydrogen. However, no coupling between these two kinds of hydrogens was observed. This could suggest that either these hydrogens do not couple at all or they couple but with such a small magnitude that it cannot easily be observed.

## D. 3,3-Dialkyl-2-carbethoxy-1,1,2-tricyanocyclopropanes and 3-aryl-2-carbethoxy-1,1,2-tricyanocyclopropanes

For preparation of 3,3-dialkyl- and 3-aryl-2-carbethoxy-1,1,2-tricyanocyclopropanes (XLIX), the following two routes were employed. The products thus prepared are listed in Table 6.

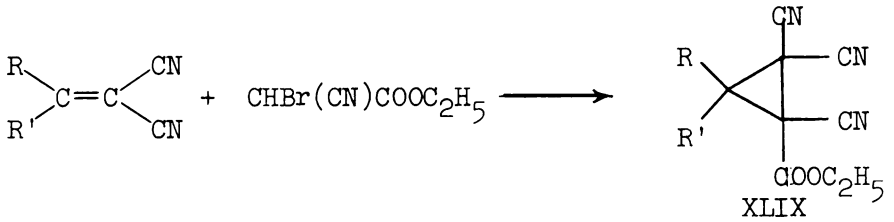
Route A



16

XLIX

Route B



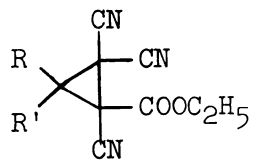
17

XLIX

Generally compounds of this group are produced in poorer yield than the corresponding tetracyanocyclopropanes. Of the two routes employed, route A produces the products quicker and in better yield than route B. Besides, several compounds that failed to form by Route B were produced by route A. The relative superiority of route A may be ascribed to the greater acidity of bromomalononitrile. Since $pK_a$ of bromomalononitrile (~5) is less than that of ethyl bromocyanoacetate (~6) (5), the concentration of anion present will be greater in the former case. Furthermore, the bromocyanocarboxycarbanion is probably bulkier than the bromodicyanocarbanion, so that its attack on the β-carbon of an ethyl alkylidenemalononitrile would be more sterically hindered.

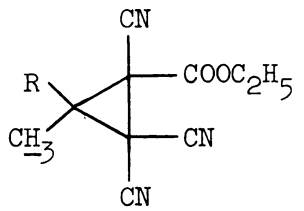
For the products (XLIX), where R ≠ R', two stereoisomers would be expected. The NMR spectra (in acetone-$d_6$) of 3-methyl-3-ethyl-2-carbethoxy-1,1,2-tricyanocyclopropane (L) and 3-methyl-3-n-propyl-2-carbethoxy-1,1,2-tricyanocyclopropane (LI) showed the cyclopropyl methyl signals at two positions, τ8.26 and τ8.39 for L and τ8.25 and τ8.38 for LI. The intensity of the two peaks in L and LI were comparable to each other. Therefore,

Table 6. 3,3-Dialkyl- and 3-Aryl-2-carbethoxy-1,1,2-tricyanocyclopropanes




| R | R' (Ar) | Route | Reaction time[a] | Yield, % |
|---|---|---|---|---|
| $CH_3$ | $CH_3$ | A | 1 hr. | 73.5 |
| | | B | 5 hrs. | 28.6 |
| $CH_3$ | $C_2H_5$ | A | 20 hrs.[b] | 63.7 |
| | | B | c | 0 |
| $CH_3$ | n-$C_3H_7$ | A | 30 days[d] | 37 |
| | | B | c | 0 |
| $CH_3$ | i-$C_3H_7$ | A | 14 days[e] | 6.46 |
| | | B | c | 0 |
| $C_2H_5$ | $C_2H_5$ | A | 2 days[f] | 35.2 |
| | | B | c | 0 |
| $(CH_2)_4$ | | A | 2 days | 14.5 |
| | | B | c | 0 |
| $(CH_2)_5$ | | A | 1 hr. | 97.5 |
| | | B | 8-9 hrs.[g] | 23.8 |
| H | $C_6H_5$ | A | 5-6 hrs.[g] | 76.7 |
| | | B | 3 hrs.[g] | 29 |
| H | p-$CH_3OC_6H_4$ | A | Overnight | 36.2 |
| | | B | 2 days | 60.3 |

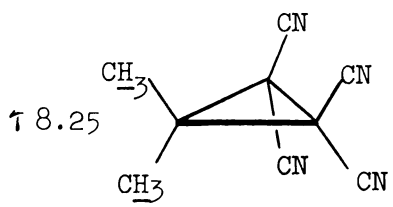
a. Time elapsed before the crystalline product separated in the reaction mixture.
b. Followed by refluxing for an additional 3 hrs.
c. Allowed to stand at room temperature for not less than a month.
d. Crystals obtained upon removing the solvent.
e. Initially refluxed for 5 hrs.
f. Followed by refluxing for an additional 6 hrs.
g. Reaction mixture was refluxed.

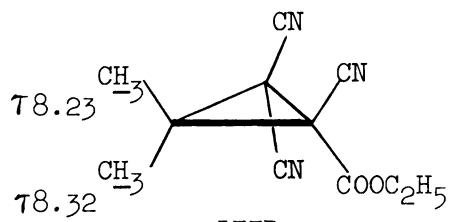



| | | | |
|---|---|---|---|
| L | R = $C_2H_5$ | $\tau$ 8.39, | $\tau$ 8.26 |
| LI | R = n-$C_3H_7$ | $\tau$ 8.38, | $\tau$ 8.25 |
| LII | R = i-$C_3H_7$ | $\tau$ 8.35, | ($\tau$ 8.25) |

these two compounds probably contained about equal amounts of the two possible stereoisomers. But the NMR spectrum (in acetone-$d_6$) of 3-methyl-3-isopropyl-2-carbethoxy-1,1,2-tricyanocyclopropane (LII) showed a very strong peak at $\tau$8.35 and only a negligibly small peak at $\tau$8.25. This suggests that only one isomer of LII was produced.

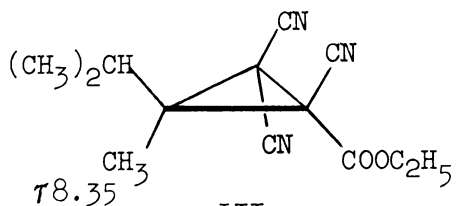
The configuration of the predominating stereoisomer of 3-methyl-3-isopropyl-2-carbethoxy-1,1,2-tricyanocyclopropane (LII) was determined as follows. In the NMR spectra (in acetone-$d_6$), the two methyls of 3,3-dimethyl-1,1,2,2-tetracyanocyclopropane appeared at $\tau$8.25 and those of 3,3-dimethyl-2-carbethoxy-1,1,2-tricyanocyclopropane (LIII) at $\tau$8.32 and $\tau$8.23.



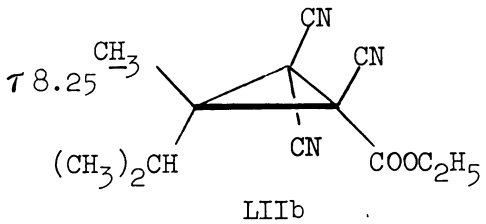




LIII

This suggests that the signal at τ8.23 in compound LIII must be due to the methyl which is cis to two cyano groups and that the signal at τ8.32 due to the methyl cis to one cyano and one carbethoxyl group. Likewise, in compounds L, LI, and LII, the signal at the higher field must be caused by the methyl cis to carbethoxyl group. Therefore, the strong methyl signal at τ8.35 of 3-methyl-3-isopropyl-2-carbethoxy-1,1,2-tricyanocyclopropane (LII) must be due to the isomer in which the methyl is cis to the carbethoxyl group (LIIa).




LIIa

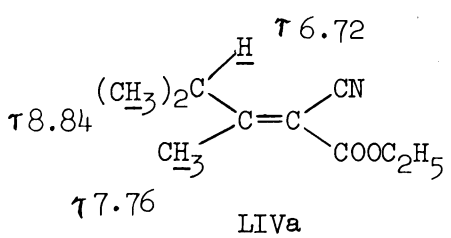



LIIb

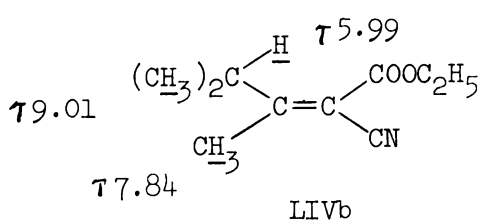
The almost exclusive formation of LIIa starting from ethyl 3-methyl-2-butylidenecyanoacetate (LIV) containing comparable amounts of both isomers* suggests that the reaction very likely proceeds through an intermediate carbanion which can undergo inversion before forming the product (see Scheme 2).

---

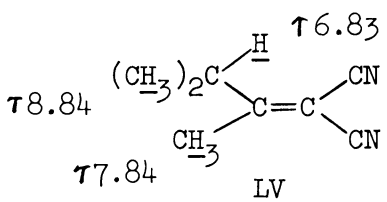
* The NMR signals for the allylic methyls of the two isomers (LIVa and LIVb) of this compound appeared at τ7.84 and τ7.76. The relative intensities of these peaks were 35:65, respectively. LIVa appears to be more favored and thus occurs in greater population (65%).




LIVa



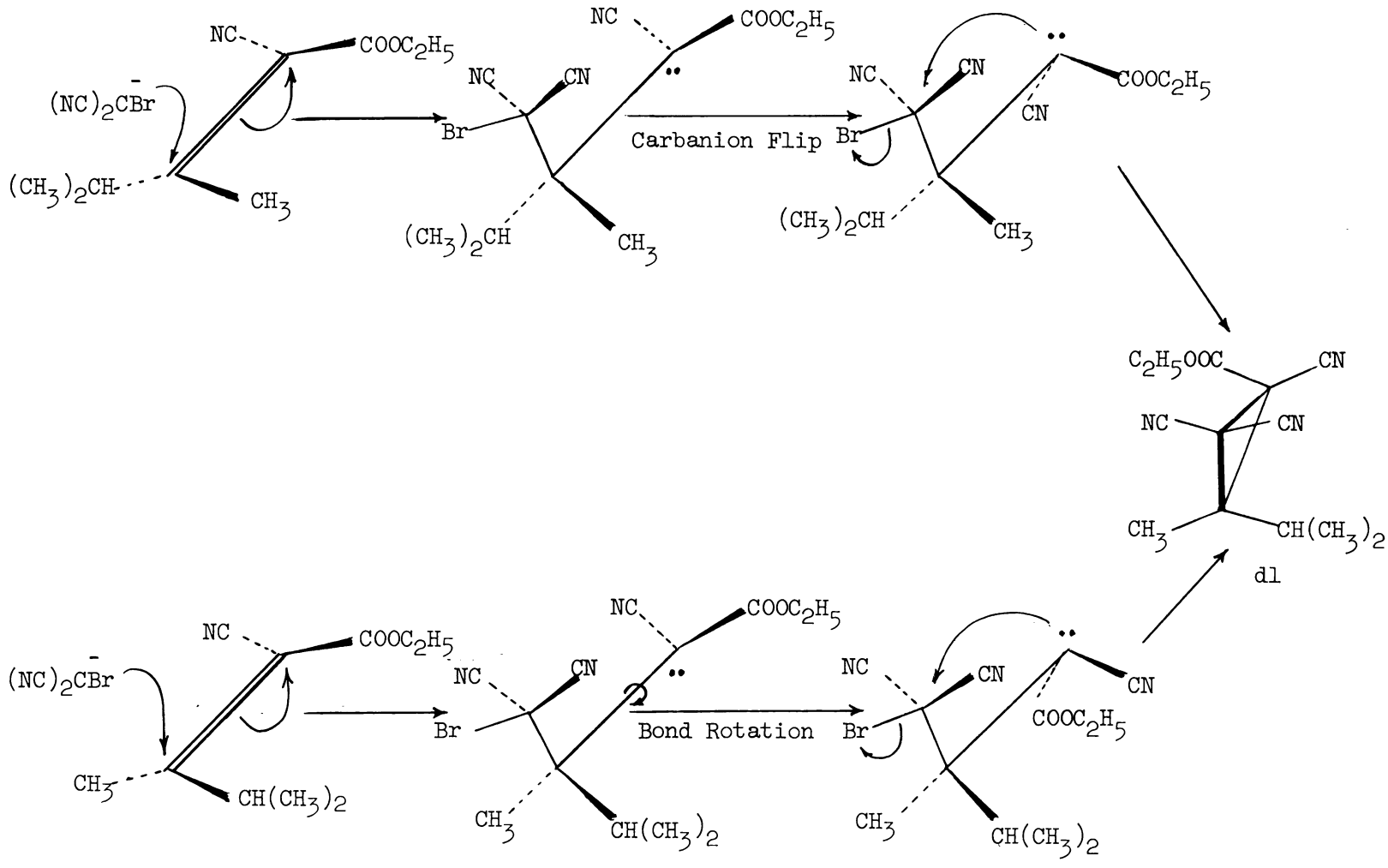

LIVb



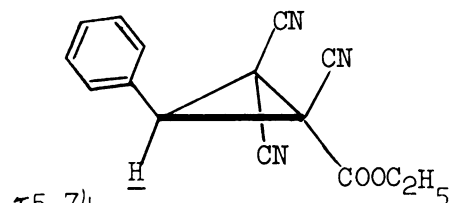

LV

Footnote continued on page 46.

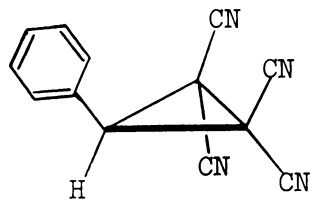
Scheme 2


NC
COOC2H5
(NC)2CBr
(CH3)2CH
CH3
Br
CN
Carbanion Flip
Bond Rotation
C2H5OOC
CH(CH3)2
dl

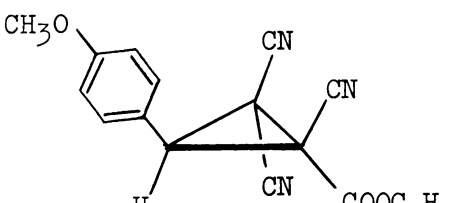
3-Phenyl-2-carbethoxy-1,1,2-tricyanocyclopropane (LVI) and its p-methoxyl derivative (LVIII) appeared to be obtained as only one stereoisomer, presumably the isomer in which the phenyl or p-methoxyphenyl is trans to the carbethoxyl.



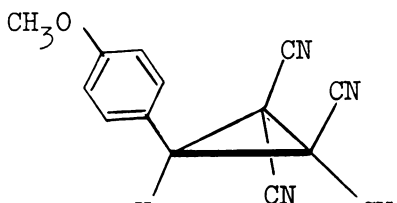

τ5.74 LVI




τ5.13 LVII




τ5.79 LVIII



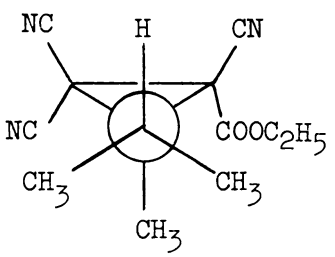

τ5.27 LIX

The cyclopropyl hydrogen of the esters, LVI (τ 5.74) and LVIII (τ 5.79) were appreciably more shielded than those of their cyano equivalents, LVII (τ 5.13) and LIX (τ 5.27), suggesting that the cyclopropyl hydrogens of the esters are likely to be cis to the carbethoxyl groups.

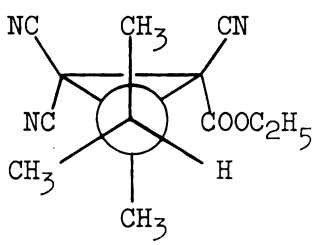
---

That the isopropyl group of LIVa is cis to the cyano group is supported by the NMR chemical shifts of both kinds of isopropyl hydrogens, τ 8.84 and τ6.72, respectively, compared to those data of LV (τ 8.84 and τ6.83, respectively). Similarly, that the allylic methyl group of LIVb is cis to the cyano group is also supported by its NMR chemical shift (τ 7.84) compared to the NMR chemical shift (τ 7.84) of LV. It is interesting to note that, in these particular compounds, the groups cis to carbethoxyl group (allylic methyl in LIVa and the methine hydrogen in LIVb) are less shielded than those cis to the cyano group (the allylic methyl in LIVb and the methine hydrogen in LIVa). A possible reason for this observation would be that, in the preferred conformation of LIVa and LIVb, the allylic methyl of LIVa and the methine hydrogen of LIVb may come close to the carbethoxyl ether oxygen.

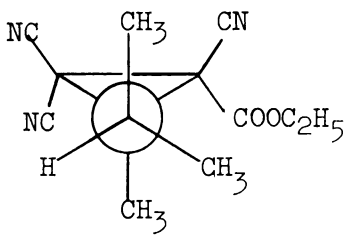
The two isopropyl methyl groups of 3-methyl-3-isopropyl-2-carbethoxy-1,1,2-tricyanocyclopropane (LII) appeared in two doublets at τ8.95 and τ8.87, respectively. Ignoring the minor stereoisomer (because of its negligibly small population) different conformers of the major isomer are shown in the Newman projections as below.




LIIc




LIId




LIIe

Conformer LIIc would probably be most stable since it holds the least number of large groups in close proximity. If LII stays most of the time in conformation LIIc, certainly two isopropyl methyls are non-equivalent with each other. Therefore, two doublets would result. This magnetic non-equivalence between two isopropyl methyl groups has been encountered and explained in terms of preferred conformation (39, 40).

## E. 3,3-Dialkyl- and 3-Aryl-2-carboxamido-1,1,2-tricyanocyclopropanes and their Reactions

### 1. Reaction of Cyclohexylidenecyanoacetamide with Bromomalononitrile

When cyclohexylidenecyanoacetamide reacted with excess of bromomalononitrile in about 80% aqueous ethanol for two days at room temperature, 7-10% of 3,3-pentamethylene-1,1,2,2-tetracyanocyclopropane (LX, identified by m.p., m.m.p., and IR spectrum) was obtained in addition to 60% of crude 3,3-pentamethylene-2-carboxamido-1,1,2-tricyanocyclopropane (LXI).

Two possible routes to the formation of LX are given in Scheme 3. In one route, cyclohexylidenecyanoacetamide first adds bromomalononitrile to form a Michael addition product LXII. LXII, eliminating bromocyanoacetamide, forms cyclohexylidenemalononitrile, which easily reacts with bromomalononitrile to form LX. The alternative route involves hydrolysis of cyclohexylidenecyanoacetamide to cyclohexanone, which reacts with bromomalononitrile to give XL (Cyclohexanone was found to react with bromomalononitrile to form LX).

The crude major product, 3,3-pentamethylene-2-carboxamido-1,1,2-tricyanocyclopropane (LXI) melts over a broad range of temperature (140-180°). On recrystallizing from boiling methanol*, the product is converted to imino amide LXIII (Scheme 3). The imino amide (LXIII) showed IR absorption bands (in nujol) at 3380 $cm^{-1}$ (NH), 2260 $cm^{-1}$ (CN), 1737 $cm^{-1}$ (CO), 1652 $cm^{-1}$, 1567 $cm^{-1}$ (both strong and broad, C=N and/or NH). The NMR spectrum (DMSO-$d_6$ at 100°) showed ring hydrogens at $\tau$8.38 and $\tau$8.10 and the N-hydrogens at $\tau$1.22 in an area ratio of 10 : 1.8. A more reliable structural proof for LXIII was provided by conversion of LXIII to LXIV by treating LXIII with hydrochloric acid. LXIV was identical with authentic sample which was synthesized from LXV by a known method (41). Conversion of LXI into LXIII is believed to involve the attack of the amide nitrogen at the cyano carbon on the vicinal position. Ring closure by means of the attack of an amide nitrogen on the cyano carbon at a vicinal position has been reported in the literature (15).

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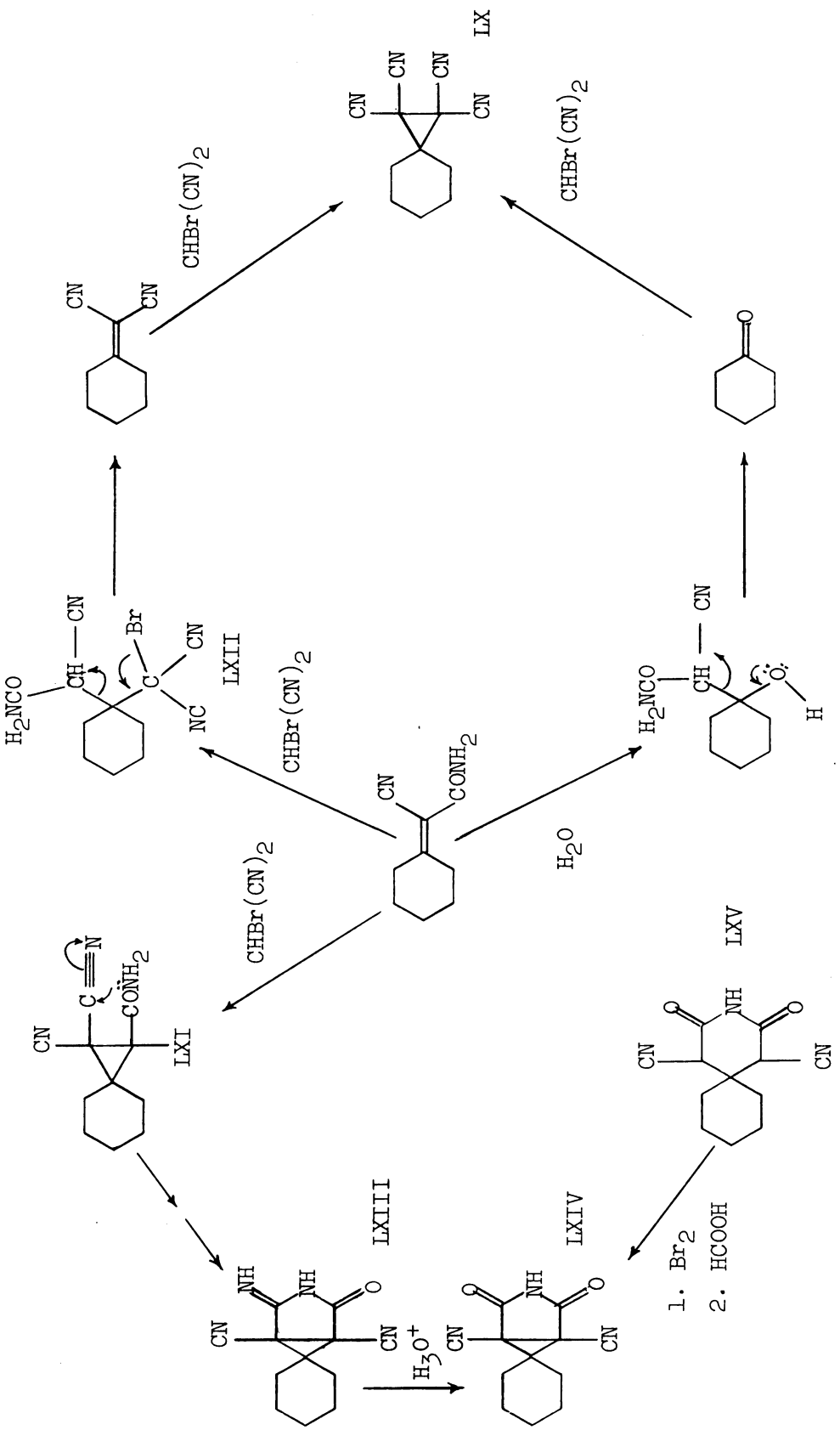
* Other organic solvents at an elevated temperature result in the same effect on LXI.

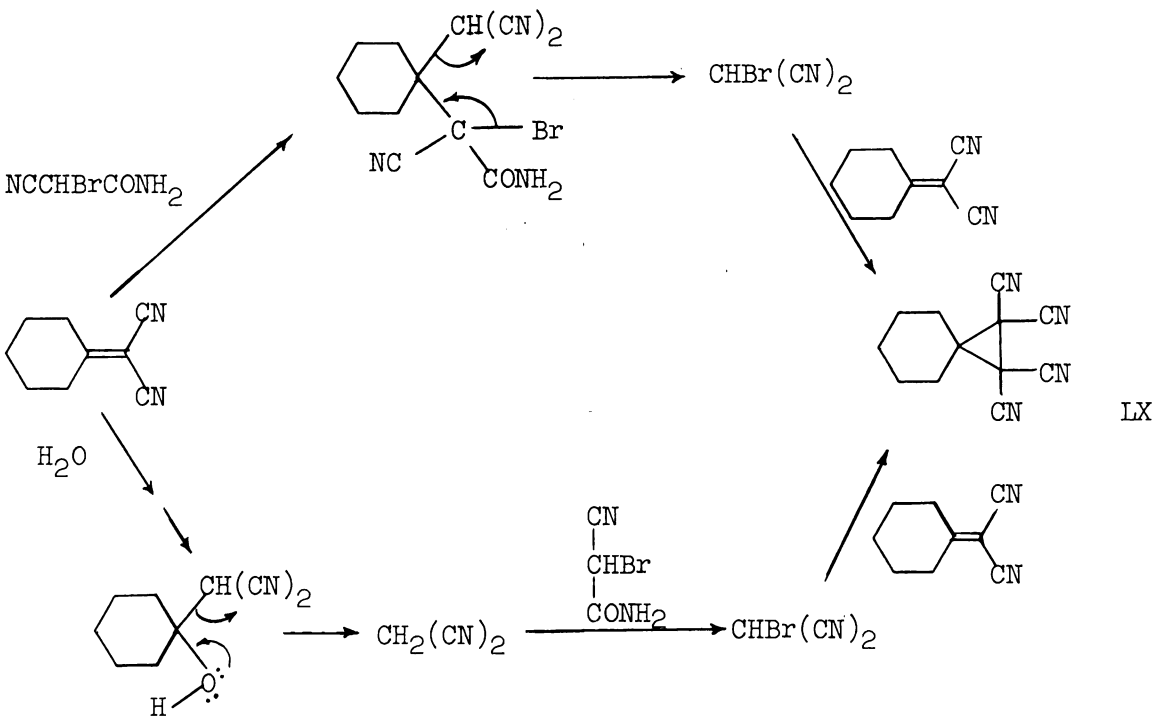
Scheme 3



2. Reaction of Cyclohexylidenemalononitrile with Bromocyanoacetamide.

When cyclohexylidenemalononitrile reacted with bromocyanoacetamide in aqueous ethanol for several days, 3,3-pentamethylene-1,1,2,2-tetracyanocyclopropane (LX) was obtained in 19.1% yield. Upon working up the reaction residue, unchanged bromocyanoacetamide was recovered. Possible mechanisms for the formation of LX are presented in Scheme 4.

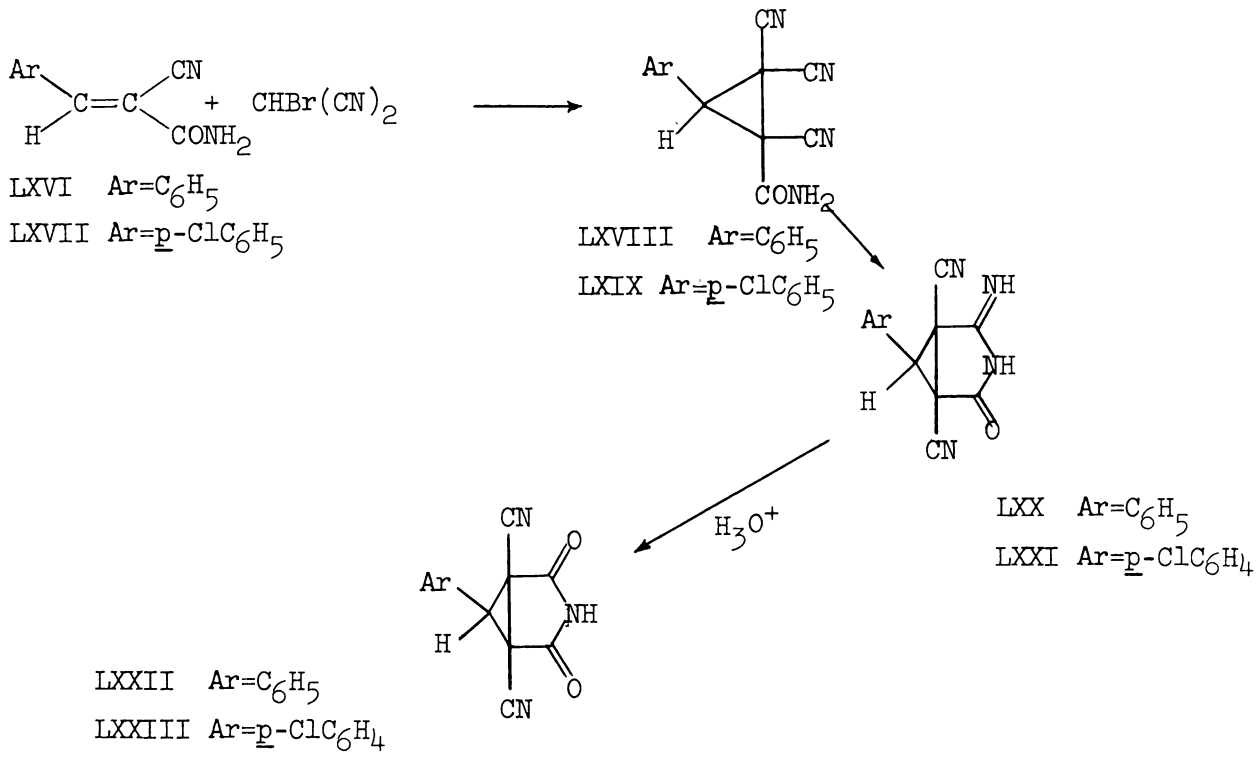
Scheme 4




3. Reaction of Arylidenecyanoacetamides with Bromomalononitrile

The reaction of some arylidenecyanoacetamides and bromomalononitrile is summarized in Scheme 5. Like 3,3-pentamethylene-2-carboxamido-1,1,2-tricyanocyclopropane (LXI), 3-phenyl-2-carboxamido-1,1,2-tricyanocyclopropane (LXVIII) and its p-chloro derivative (LXIX), on heating, were exclusively converted into the imino amides LXX and LXXI, respectively.

Scheme 5




Treatment of LXX and LXXI with hydrochloric acid yielded the carboximido compounds, LXXII and LXXIII, respectively. (3-p-Methoxyphenyl-2-carboxamido-1,1,2-tricyanocyclopropane produced a mixture of compounds which could not be identified.)

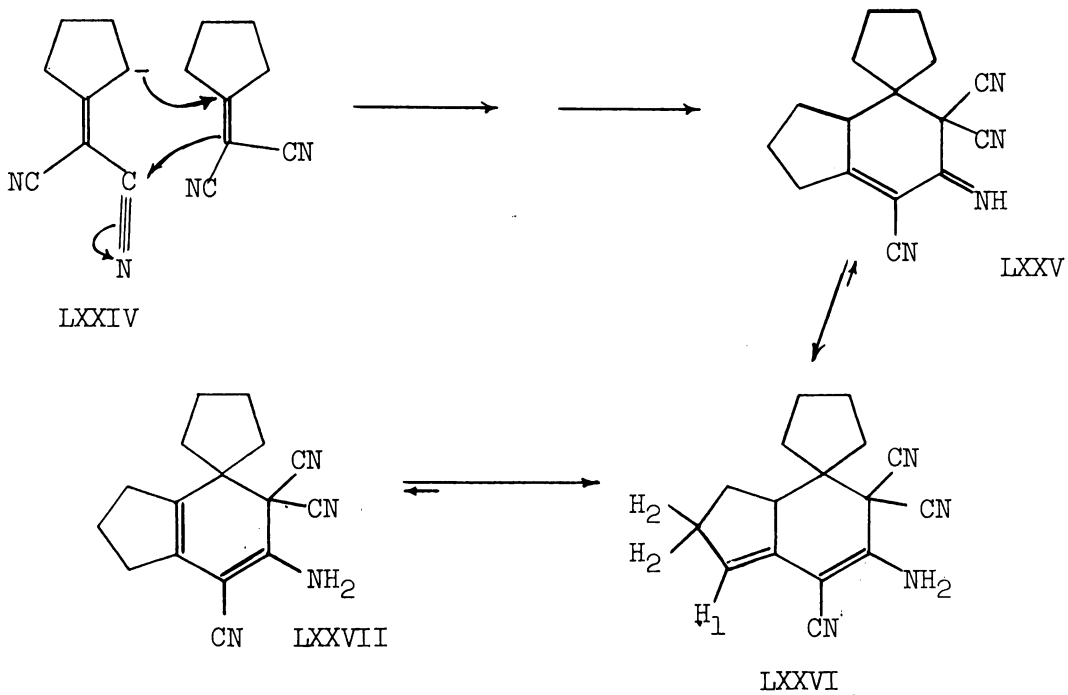
F. Some Dimers of Alkylidenemalononitriles

It was observed that cyclopentylidenemalononitrile (LXXIV), on treating with pyridine, gave light yellow crystals, m.p. 187-190°. This crystalline product had also been formed (in the distillation flask) while distilling LXXIV. Analysis gave an empirical formula $(C_8H_8N_2)_n$. Since a number of alkylidenemalononitriles are known to dimerize (42, 43, 44), this compound was suspected of being cyclopentylidenemalononitrile dimer $C_{16}H_{16}N_4$. The IR spectrum (in nujol) showed the presence of $NH_2$ (3440 $cm^{-1}$, 3370 $cm^{-1}$, 3260 $cm^{-1}$)

and CN (2240 $cm^{-1}$). The absorption bands at 1650 $cm^{-1}$ and 1589 $cm^{-1}$ could be ascribed to C=C and/or NH. The NMR spectrum (in DMSO-$d_6$) showed three multiplets at $\tau$8.23, $\tau$7.61, and $\tau$6.91, a doublet (J = 1.8 c.p.s.) at $\tau$4.52 and a singlet at $\tau$2.72 in an area ratio of (three multiplets as 13) 13 : 0.97 : 1.89. The UV spectrum (in ethanol) showed absorption bands at 308 mμ (ε 12,226), 241 mμ (ε 8,681), 224 mμ (ε 6,639), and 215 mμ (shoulder).

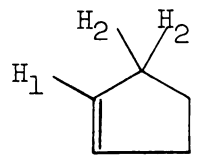
A mechanism similar to the one advanced for the formation of the isopropylidenemalononitrile dimer (42) can be applied to account for the formation of cyclopentylidenemalononitrile dimer (Scheme 6). Structures LXXV and LXXVII are eliminated because the NMR spectrum showed a hydrogen in the vinyl region ($\tau$ 4.52)*. The NMR signal at $\tau$4.52 is a doublet,

Scheme 6



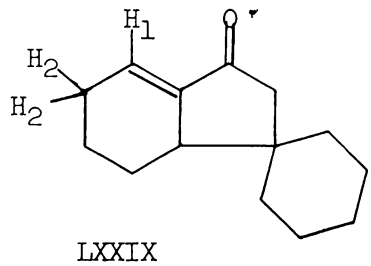

* If the compound is a mixture of these three isomers, the percentage of LXXV and LXXVII must be negligibly small.

J = 1.8 c.p.s., although it is expected to be a triplet for LXXVI. Examination of a model of LXXVI reveals that the two dihedral angles between $H_1$ and two $H_2$'s are not the same. One is almost 90° whereas the other is approximately 45-60°. Only the $H_2$ with a dihedral angle ~45-60° should split $H_1$. Therefore only a doublet would be observed for $H_1$. The magnitude of $J_{H_1, H_2}$ (dihedral angle ~45-60°) = 1.8 c.p.s. (for LXXVI) is favorably compared to that of $J_{H_1, H_2}$ (dihedral angle 63°) = 2.1 c.p.s. observed for cyclopentene LXXVIII (45). A precedent in which a vinyl hydrogen coupled to only one of two neighbouring




LXXVIII

methylene hydrogens was encountered, i.e., compound LXXIX showed $H_1$ at τ3.45 (in $CCl_4$) as a doublet, J = 3.5 c.p.s. (46).




LXXIX

Isopropylidenemalononitrile dimer (LXXX), m.p. 171-174°, and 2-butylidenemalononitrile dimer (LXXXI), m.p. 167-169°, were prepared by treating the corresponding monomer with pyridine. They were also formed (in the distillation flask) while distilling the corresponding monomers*.

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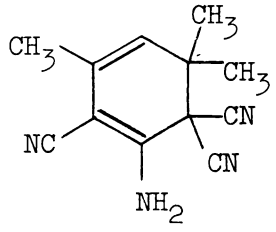
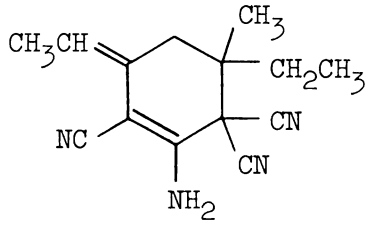
* Isopropylidenemalononitrile dimer was also found to form while storing the monomer at room temperature for a few months.

Data for these dimers agreed with those reported in the literature (42,44).



LXXX

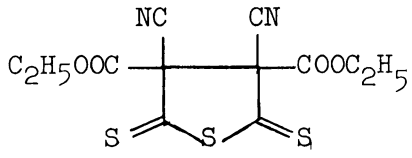


LXXXI

G. Miscellaneous

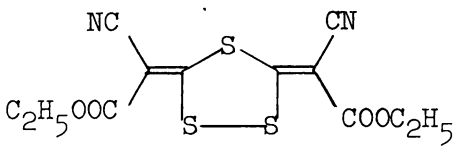
1. Sulfur-containing Compound obtained from Ethyl Sodiocyanoacetate and Carbon Disulfide

In an attempt to prepare ethyl bromocyanoacetate according to a reported method (47), dry ethyl sodiocyanoacetate suspended in carbon disulfide was allowed to react with bromine. Instead of the desired ethyl bromocyanoacetate, there was obtained a yellow compound, m.p. 232-236° (from benzene). Analysis gave an empirical formula $C_{12}H_{10}N_2O_4S_3$. The IR spectrum (in nujol) showed the absorption bands at 2210 $cm^{-1}$ (CN), 1661 $cm^{-1}$ (CO), 1181 $cm^{-1}$ (ester band?) The NMR spectrum (in DMSO-$d_6$ at 80°) showed only a triplet at $\tau$8.62 and a quartet at $\tau$5.60. The UV spectrum (in acetonitrile) gave only one peak at 334 m$\mu$ ($\epsilon$ 27,600). Compound $C_{12}H_{10}N_2O_4S_3$ rapidly decolorized potassium permanganate solution but did not decolorize bromine appreciably. Structure LXXXII had been assigned to this compound by Wenzel who first prepared this compound by the identical procedure. However, some of the observed data do not satisfy structure

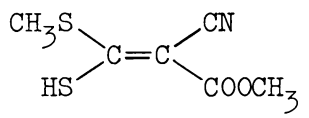


LXXXII

LXXXII. For example, the IR bands at 2210 $cm^{-1}$ is strongly indicative of a conjugated cyano group and is too low for the cyano group of LXXXII. Besides, LXXXII would not decolorize potassium permanganate so rapidly. Therefore another structure LXXXIII is proposed for this compound (stereochemistry is not known). The IR spectrum of LXXXIV showed bands at 2209 $cm^{-1}$ for C≡N and 1669 $cm^{-1}$ for $COOCH_3$ (49). These values are close to 2210 $cm^{-1}$ (CN) and 1661 $cm^{-1}$ ($COOC_2H_5$) of LXXXIII and seem to suggest the presence of $-S)_2C{=}C(CN)COOC_2H_5$ moiety in the molecule. It is reported that methyl sodiocyanoacetate, on treating with

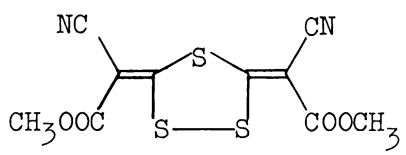


LXXXIII



LXXXIV

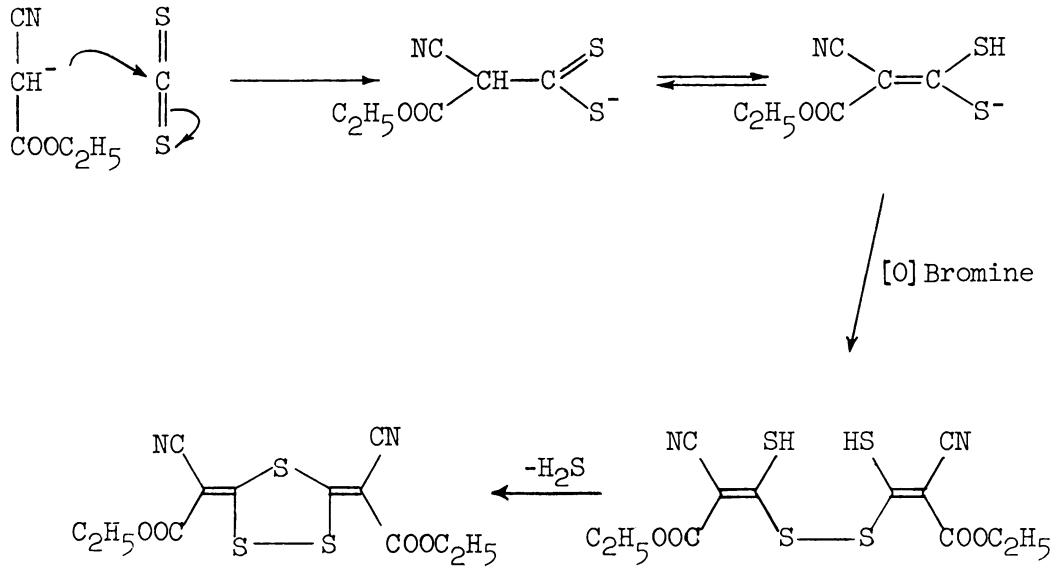
carbon disulfide followed by oxidation with ammonium peroxysulfate, produced compound LXXXV (49). Assignment of the structure was based on the low frequency of C≡N absorption band in IR spectrum (data not given).



LXXXV

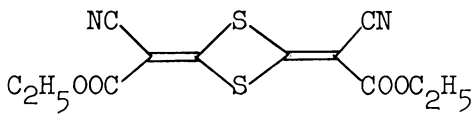
A possible mechanism for the formation of LXXXIII is proposed in Scheme 7.

Scheme 7




LXXXIII

Oxidation of LXXXIII ($C_{12}H_{10}N_2O_4S_3$) using potassium permanganate in acetone, produced a new compound, $C_{12}H_{10}N_2O_4S_2$, m.p. 177-179° (from an acetone-ethanol mixture). The IR spectrum (in nujol) showed absorption bands at 2230 $cm^{-1}$ (CN), 1696 $cm^{-1}$ (CO), 1560 $cm^{-1}$ (C=C), 1188 $cm^{-1}$ (ester band?), and the UV spectrum (in ethanol) showed three absorption bands at 215 m$\mu$ ($\epsilon$ 16,735), 333 m$\mu$ ($\epsilon$ 48,345), and 348 m$\mu$ ($\epsilon$ 52,804). Structure LXXXVI is proposed for this compound (stereochemistry not known).



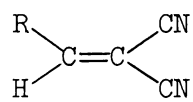

LXXXVI

An attempted reduction of LXXXIII using lithium aluminum hydride or sodium borohydride gave an unidentified residue. Also, desulfurization of LXXXIII using Raney nickel was tried, but there was obtained a dark liquid residue with an amine odor, which could not be identified.

2. Reaction of 2-Methyl-1-nitropropene with Bromomalononitrile

Reaction of 2-methyl-1-nitropropene (above 85% pure as determined by the NMR and v.p.c.) and bromomalononitrile in aqueous ethanol produced two compounds $C_{10}H_7BrN_4$ (white crystals, m.p. 201-202°) and $C_7H_8N_4O_3$ (yellow crystals, m.p. 251-252°). The white compound crystallized out first and, several hours later, the yellow compound followed.

Compound $C_{10}H_7BrN_4$ showed C≡N band at 2290 $cm^{-1}$ in the IR (in nujol) spectrum. The compound did not have absorption for the entire accessible UV and Visible range (in ethanol). The NMR spectrum (in acetone-$d_6$) showed two singlets at τ 7.78 and τ 5.68 in an area ratio of 6 : 1. Three possible structures LXXXVII, LXXXVIII, and LXXXIX are proposed for this compound and a possible mechanism for the formation of each of them is shown in Scheme 8. Structure LXXXVIII was eliminated for the following three reasons. (i) The compound was transparent in the UV and Visible, whereas alkylidenemalononitriles absorb intensely between 230-250 mμ (due to >C=C($CN_2$). (ii) The NMR singlet at 5.68 is too high for the vinyl hydrogen in a compound of type XC, which usually appears between τ 1.00 and τ 3.00 depending on the nature of R group. (iii) The IR spectrum lacked



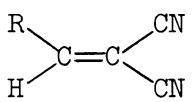

XC

absorption in the double bond region. Structure LXXXVII was also eliminated because the NMR singlet at τ 7.78 is not compatible with two geminal methyl groups, which should appear as two separate peaks.

2. Reaction of 2-Methyl-1-nitropropene with Bromomalononitrile

Reaction of 2-methyl-1-nitropropene (above 85% pure as determined by the NMR and v.p.c.) and bromomalononitrile in aqueous ethanol produced two compounds $C_{10}H_7BrN_4$ (white crystals, m.p. 201-202°) and $C_7H_8N_4O_3$ (yellow crystals, m.p. 251-252°). The white compound crystallized out first and, several hours later, the yellow compound followed.

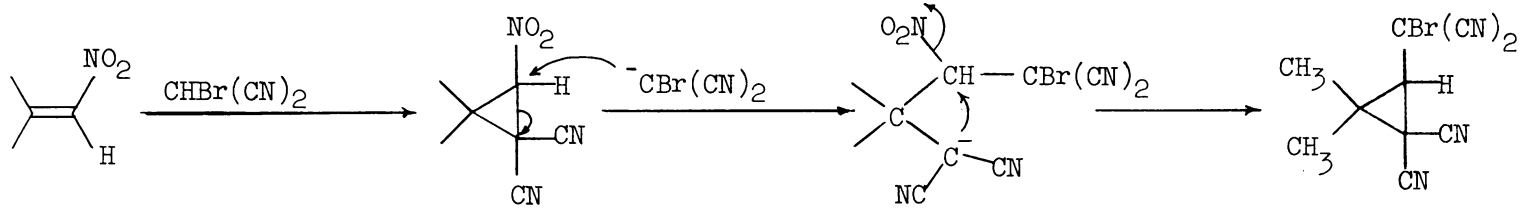
Compound $C_{10}H_7BrN_4$ showed C≡N band at 2290 $cm^{-1}$ in the IR (in nujol) spectrum. The compound did not have absorption for the entire accessible UV and Visible range (in ethanol). The NMR spectrum (in acetone-$d_6$) showed two singlets at τ7.78 and τ5.68 in an area ratio of 6 : 1. Three possible structures LXXXVII, LXXXVIII, and LXXXIX are proposed for this compound and a possible mechanism for the formation of each of them is shown in Scheme 8. Structure LXXXVIII was eliminated for the following three reasons. (i) The compound was transparent in the UV and Visible, whereas alkylidenemalononitriles absorb intensely between 230-250 mμ (due to >C=C(CN$_2$). (ii) The NMR singlet at 5.68 is too high for the vinyl hydrogen in a compound of type XC, which usually appears between τ1.00 and τ3.00 depending on the nature of R group. (iii) The IR spectrum lacked




XC

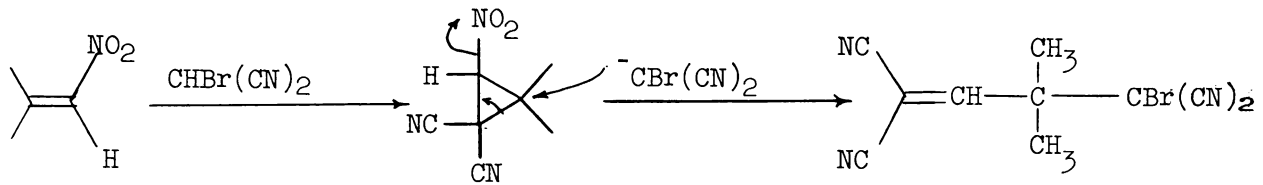
absorption in the double bond region. Structure LXXXVII was also eliminated because the NMR singlet at τ7.78 is not compatible with two geminal methyl groups, which should appear as two separate peaks.

Scheme 8



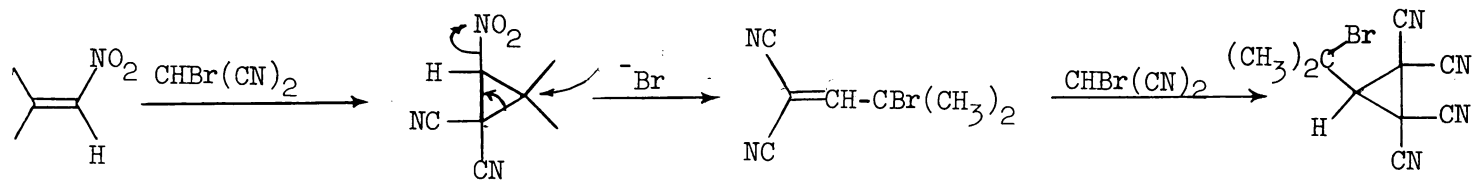
LXXXVII

8A



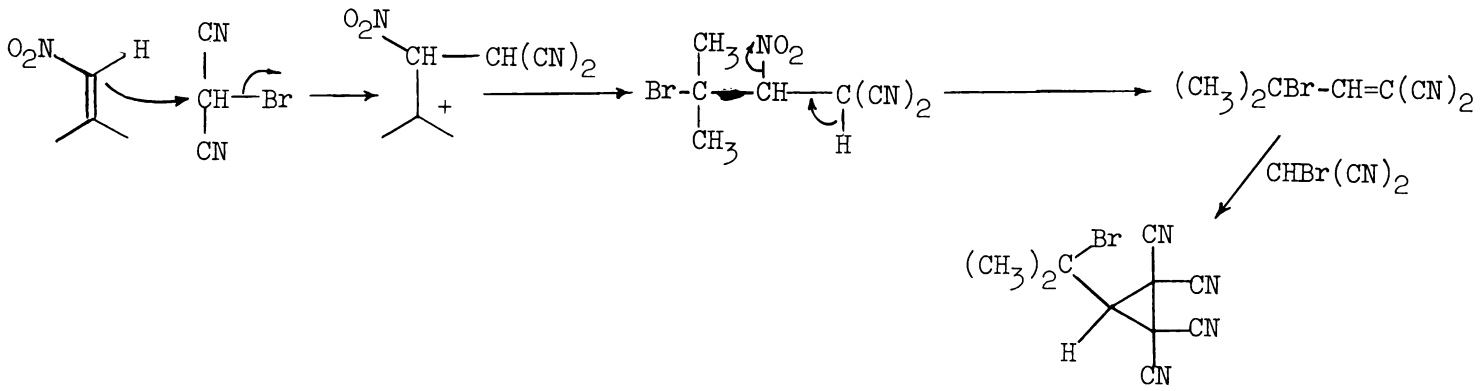
LXXXVIII

8B



LXXXIX

8C



LXXXIX

8D

Structure LXXXIX agrees well with all the spectral data obtained. When propane, with $\tau CH_3$ = 9.10 (50), is converted into 2-bromopropane, with $\tau CH_3$ = 8.29 (51), the magnitude of the deshielding effect caused by bromine on the vicinal hydrogens is 0.81 p.p.m. Now, 3-isopropyl-1,1,2,2-tetracyanocyclopropane shows the two isopropyl methyl groups at $\tau$ 8.63 and the cyclopropyl hydrogen at $\tau$6.50 (in acetone-$d_6$) (28). If this vicinal bromine effect is applied, then the expected chemical shifts for two methyls and the cyclopropyl hydrogen in LXXXIX would be $\tau$(8.63 - 0.81) or $\tau$7.82 and $\tau$(6.50 - 0.81) or $\tau$5.69, respectively. These expected values are close to the observed values of $\tau$7.78 and $\tau$5.68, respectively. The transparency in UV and the high C≡N frequency in IR agree with structure LXXXIX. Thus it is very likely that compound $C_{10}H_7BrN_4$ is 3-(2'-bromoisopropyl)-1,1,2,2-tetracyanocyclopropane (LXXXIX). Of the two possible mechanisms proposed for the formation of LXXXIX (see Scheme 8C and 8D), 8D seems to be less likely because the carbonium ion may not be stable.

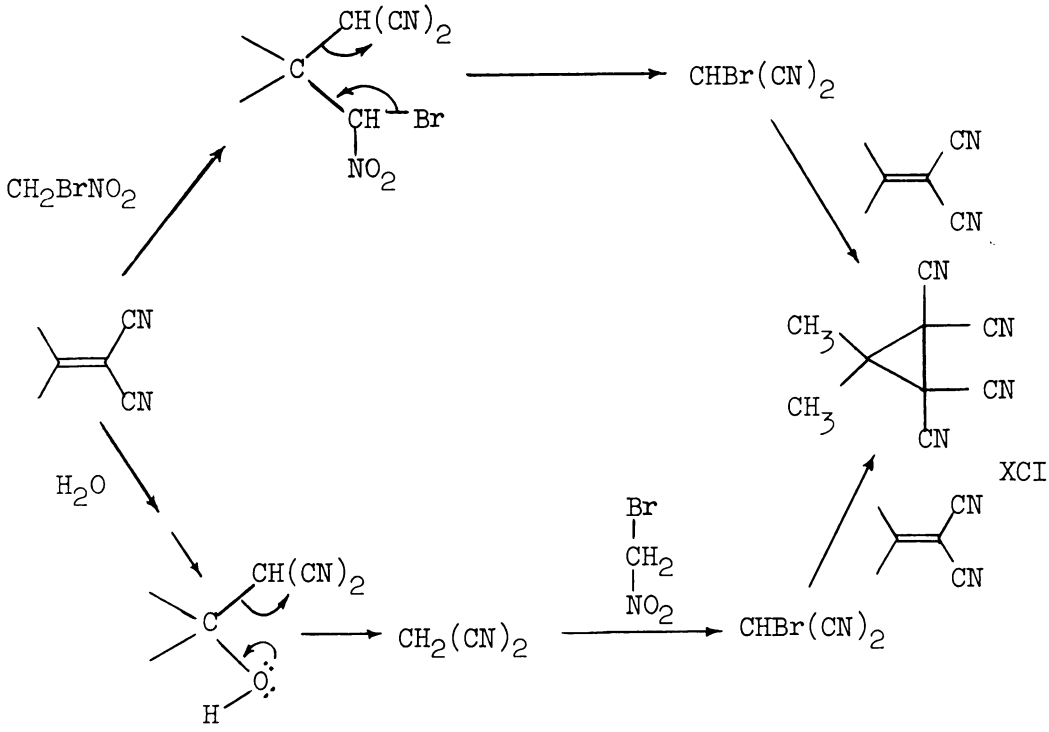
The yellow compound $C_7H_8N_4O_3$ showed IR absorption bands (in nujol) at 3350 $cm^{-1}$, 3245 $cm^{-1}$, 3175 $cm^{-1}$, 2255 $cm^{-1}$, 1659 $cm^{-1}$, 1585 $cm^{-1}$, 1536 $cm^{-1}$. Two peaks appeared in the NMR spectrum (in DMSO-$d_6$) at $\tau$8.49 (s) and $\tau$1.02 (broad), respectively, in an area ratio of 6 : 1.82. These data suggest an amide for this compound. However, a plausible structure has not yet been deduced for this product.

3. Reaction of Isopropylidenemalononitrile with Bromonitromethane

When isopropylidenemalononitrile was allowed to react with bromonitromethane, a small amount of 3,3-dimethyl-1,1,2,2-tetracyanocyclopropane (XCI) was obtained instead of the desired product, 3,3-dimethyl-2-nitro-1,1-dicyanocyclopropane.

Two possible mechanisms for the formation of XCI are shown in Scheme 9.

Scheme 9



# EXPERIMENTAL

## A. General Procedures

Unless otherwise specified, all IR spectra were obtained on a Unicam S P· 200 Infrared Spectrophotometer and the absorption bands were expressed in $cm^{-1}$ ($\mu$); all UV spectra were obtained on a Beckman DB Spectrophotometer and the absorption bands were expressed in m$\mu$ ($\epsilon$); all NMR spectra were obtained on a Varian A-60 Spectrometer using tetramethylsilane as an internal standard and the signal positions were expressed in $\tau$ units.

All melting points were taken in a sealed capillary tube and were uncorrected. All microanalyses were performed by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

## B. Starting Materials

All compounds described in this section were identified by IR, UV, and NMR spectra (as far as possible) and by comparing the physical data such as b.p., m.p., refractive index, etc. with those reported in the literature (in case the compounds were known).

### 1. Bromomalononitrile

Prepared from malononitrile and bromine (28).

### 2. Ethyl Bromocyanoacetate

Prepared from ethyl cyanoacetate and bromine (52).

### 3. Ethyl Bromonitroacetate

Prepared from ethyl nitroacetate and bromine in the same manner

described for the preparation of ethyl bromocyanoacetate, $b_4$ 79-80°. NMR (neat): $\tau$ 8.64 (t), $C\underline{H}_3CH_2O$, $\tau$ 5.62 (q), $CH_3C\underline{H}_2O$, $\tau$ 3.40 (s), $O_2NC\underline{H}Br$.

4. Ethyl Nitroacetate

Prepared from ethyl acetoacetate, acetic anhydride, and fuming nitric acid (53), $b_6$ 91°, $n_D^{24}$ 1.4220. NMR (neat): $\tau$ 8.70 (t), $C\underline{H}_3CH_2O$; $\tau$ 5.70 (q), $CH_3C\underline{H}_2$ ; $\tau$ 4.72 (s), $O_2NC\underline{H}_2$.

5. Bromocyanoacetamide

Prepared from dibromocyanoacetamide and cyanoacetamide (54), m.p. 114-117°. NMR (in acetone) showed two singlets at $\tau$ 4.58 and $\tau$ 2.64 in an area ratio of 0.94 : 2.

6. Dibromocyanoacetamide

Prepared from cyanoacetamide and bromine (55), m.p. 121-124°.

7. Dibromoacetonitrile

Prepared from ethyl cyanoacetate, bromine, and magnesium oxide (56), $b_{20}$ 70-73°, $n_D^{24}$ 1.5394. NMR (neat): $\tau$ 4.13 (s).

8. Bromonitromethane

Prepared from nitromethane, bromine and barium oxide (57), b. 145-150°. NMR (neat): $\tau$ 4.17 (s).

9. Alkylidenemalononitriles

Isopropylidenemalononitrile and 3,3-dimethyl-2-butylidenemalononitrile were prepared according to the procedure described by Frout (58). All other alkylidenemalononitriles were prepared in the manner described by Cope and Hancock for the preparation of ethyl 3-pentylidenecyanoacetate (59).

10. Ethyl Alkylidenecyanoacetates

Ethyl isopropylidenecyanoacetate was prepared according to the procedure described by Frout (58). All other ethyl alkylidenecyanoacetates were prepared in the manner described by Cope and Hancock for the preparation of ethyl 3-pentylidenecyanoacetate (59).

11. Arylidenemalononitriles

p-Methylbenzylidenemalononitrile was prepared in the manner described by Cope and Hancock for the preparation of ethyl 3-pentylidenecyanoacetate (59). All other benzylidenemalononitriles were prepared according to the procedure of Corson and Stoughton (60).

12. β-Arylalkylidenemalononitriles

Prepared in the manner described by Cope and Hancock for the preparation of ethyl 3-pentylidenecyanoacetate (59).

13. Miscellaneous

Ethyl benzylidenecyanoacetate (61), ethyl p-methoxybenzylidenecyanoacetate (60), benzylidenecyanoacetamide (62), p-methoxybenzylidenecyanoacetamide (63), and p-chlorobenzylidenecyanoacetamide (62) were prepared according to the procedure reported previously. 2,3-Benzocyclopentylidenecyanoacetamide and 2,3-benzocyclohexylidenecyanoacetamide were prepared in the manner described by Cope and Hancock for the preparation of ethyl 3-pentylidenecyanoacetate (59).

C. Preparation of 3,3-Dialkyl-1,1,2,2-tetracyanocyclopropanes

1. 3,3-Dimethyl-1,1,2,2-tetracyanocyclopropane

Method I. In a 50-ml. Erlenmeyer flask were placed 0.5 g. (4.72 mmoles) of isopropylidenemalononitrile and 5 ml. of 50% aqueous ethanol. To this

solution was added 1 g. (6.90 mmoles) of bromomalononitrile. A precipitate formed within 2 mins. After one-half hr., the crystals were collected by means of filtration and recrystallized from an ethanol-acetone mixture, m.p. 206-208° (lit. val. (1) 209.5-210°), 0.69 g. (86%). The IR and NMR spectra agreed with those obtained previously (28).

This reaction was found to proceed also in 50% aqueous acetone (71%) and in 95% ethanol (68.2%) and more slowly in water (72%).

Method II. In a 50-ml. Erlenmeyer flask was dissolved 0.5 g. (3.45 mmoles) of bromomalononitrile in 10 ml. of 50% aqueous acetone. The solution was kept at room temperature for 24 hrs. A white precipitate that had formed was worked up as described in Method I, m.p. 204-206°, 0.23 g. (78.3%).

2. 3-Methyl-3-ethyl-1,1,2,2-tetracyanocyclopropane

One gram (8.3 mmoles) of 2-butylidenemalononitrile and 1.45 g. (10.0 mmoles) of bromomalononitrile were dissolved in 15 ml. of 80% aqueous ethanol. Crystals formed within a few mins. After a few hrs., the crystals were filtered and recrystallized from an ethanol-acetone mixture, m.p. 204-206° (lit. val. (3), 202-202.5°), 1.39 g. (91%). IR (in nujol): 2265 (4.42),CN; 982 (10.18), cyclopropane ring (?). NMR (in acetone-$d_6$): $\tau$ 8.72 (t), $CH_2\underline{CH_3}$; $\tau$ 8.23 (s), ring methyl; $\tau$ 7.92 (q), $\underline{CH_2}CH_3$.

3. 3-Methyl-3-n-propyl-1,1,2,2-tetracyanocyclopropane

Eight-tenths gram (5.95 mmoles) of 2-pentylidenemalononitrile and 1.3 g. (8.97 mmoles) of bromomalononitrile were dissolved in 20 ml. of 75% aqueous ethanol. The precipitate which had formed in a few mins. was filtered and recrystallized from ethanol, m.p. 164-166° (lit. val. (4), 167.5-168°), 1.15 g. (97.5%). IR (in nujol): 2280 (4.39), CN; 983 (10.17),

cyclopropane ring (?). NMR (in acetone-$d_6$); $\tau$ 8.94 (t), $C\underline{H}_3CH_2CH_2$; $\tau$ 8.23 (s), ring methyl; $\tau$ 8.07 (m), $CH_3(C\underline{H}_2)_2$.

4. 3-Methyl-3-isopropyl-1,1,2,2-tetracyanocyclopropane

Five-tenths gram (3.73 mmoles) of 3-methyl-2-butylidenemalononitrile and 0.87 g. (6.00 mmoles) of bromomalononitrile were mixed in 12 ml. of 80% aqueous ethanol. A precipitate started forming in 1 hr. After a few hrs., the first crop was collected and after 24 hrs., the second crop was collected. To the filtrate obtained after removal of the second crop was added an additional 0.87 g. (6.00 mmoles) of bromomalononitrile. Thereafter crystals were collected every 24 hrs. for 5 days. Total yield, after recrystallization from ethanol, amounted to 0.72 g. (97.4%), m.p. 201-202.5° (lit. val. (4), 187-188°). IR (in nujol): 2260 (4.42), CN; 983 (10.17), cyclopropane ring (?). NMR (in DMSO-$d_6$): $\tau$ 8.82 (d), $(C\underline{H}_3)_2CH$; $\tau$ 8.49 (s), ring methyl; $\tau$ 8.32 (septet), $(CH_3)_2C\underline{H}$.

5. 3-Methyl-3-n-pentyl-1,1,2,2-tetracyanocyclopropane

2-Heptylidenemalononitrile (1.25 g., 7.71 mmoles) and bromomalononitrile (1.45 g., 10.0 mmoles) were dissolved in 10 ml. of 90% aqueous ethanol. A precipitate formed in 1 hr., which was filtered after a few hrs. Recrystallization from ethanol yielded 1.70 g. (97.5%) of white crystals, m.p. 103-105°. IR (in nujol): 2280 (4.38), CN; 982 (10.18), cyclopropane ring (?) NMR (in DMSO-$d_6$): $\tau$ 9.08 (t), $C\underline{H}_3(CH_2)_3CH_2$; $\tau$ 8.73 (m), $CH_3(C\underline{H}_2)_3CH_2$; $\tau$ 8.41 (s), ring methyl; $\tau$ 8.27 (m), $CH_3(CH_2)_3C\underline{H}_2$.

Anal. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.28; N, 24.76

Found: C, 69.14; H, 6.37; N, 24.78

6. 3-3-Diethyl-1,1,2,2-tetracyanocyclopropane

Method I. 3-Pentylidenemalononitrile (1.35 g., 10.1 mmoles) and

bromomalononitrile (2.00 g., 13.8 mmoles) were dissolved in 15 ml. of ethanol. A precipitate formed in a few hrs. and was filtered after standing for an additional several hrs. Recrystallization from ethanol gave 1.75 g. (88.5%) of white crystals, m.p. 163-165° (lit. val. (4), 167-168°). IR (in nujol): 2276 (4.39), CN; 980 (10.20), cyclopropane ring (?). NMR (in acetone-$d_6$): $\tau$ 8.76 (t), $CH_3CH_2$; $\tau$ 7.96 (q), $CH_3CH_2$.

Method II. In a 50-ml. Erlenmeyer flask were placed 0.86 g. (10.0 mmoles) of 3-pentanone, 1.00 g. (6.9 mmoles) of bromomalononitrile, and 10 ml. of 50% aqueous ethanol. The reaction mixture was shaken until a complete solution was obtained and set at room temperature for a month (actually the time required for reaction may not have been this long). Then the contents in the flask were transferred to a beaker, when the product crystallized out. Recrystallization from ethanol yielded 0.32 g. (46.8%) of white crystals melting at 165-166°.

7. 3-Ethyl-3-n-butyl-1,1,2,2-tetracyanocyclopropane

One gram (6.17 mmoles) of 3-heptylidenemalononitrile and 1.5 g. (10.3 mmoles) of bromomalononitrile were dissolved in 15 ml. of 90% ethanol and set aside for 24 hrs. The precipitate which had formed was filtered and, upon recrystallization from ethanol, yielded 1.32 g. (94.5%) of white crystals, m.p. 119-121°. IR (in nujol): 2275 (4.40), CN; 998 (10.02), cyclopropane ring (?). NMR spectrum (in acetone-$d_6$) showed an irresolvable complex multiplet from $\tau$ 9.10 to $\tau$ 8.00.

Anal. Calcd. for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76

Found: C, 68.97; H, 6.27; N, 24.85

8. 3,3-Dicyclopropyl-1,1,2,2-tetracyanocyclopropane

Dicyclopropylmethylenemalononitrile (0.79 g., 5.0 mmoles) and bromo-

malononitrile (1.00 g., 6.9 mmoles) were dissolved in 20 ml. of 60% aqueous ethanol. A precipitate formed in 10 mins. The first crop was collected after a few hrs. and the second crop after standing overnight. Recrystallization from ethanol yielded 0.69 g. (62%) of fluffy crystals, m.p. 185-187°. IR (in nujol): 2262 (4.42), CN; 1040 (9.62), cyclopropane ring (?). NMR spectrum (in acetone-$d_6$) showed two multiplets at $\tau$ 9.09 and $\tau$ 8.76.

Anal. Calcd. for $C_{13}H_{10}N_4$: C, 70.25; H, 4.54; N, 25.21

Found: C, 70.38; H, 4.47; N, 25.32

9. 3,3-Tetramethylene-1,1,2,2-tetracyanocyclopropane

One gram (7.57 mmoles) of cyclopentylidenemalononitrile and 1.5 g. (10.3 mmoles) of bromomalononitrile were dissolved in 14 ml. of 85% aqueous ethanol. The precipitate which had formed in 30 mins. was filtered after standing for a few hrs., and, upon recrystallization from acetone, yielded 0.78 g. (52.6%) of greyish white crystals, m.p. 240-243° dec. (lit. val. (4), 239-240°). IR (in nujol): 2270 (4.41), CN; 968 (10.33), cyclopropane ring (?). The NMR spectrum (in DMSO-$d_6$ at about 110°) showed a broad peak at $\tau$ 7.91 with reference to nitromethane ($\tau$ 5.67) as an internal standard.

10. 3,3-Pentamethylene-1,1,2,2-tetracyanocyclopropane

Method I. One gram (6.84 mmoles) of cyclohexylidenemalononitrile and 1.7 g. (11.07 mmoles) of bromomalononitrile were dissolved in 15 ml. of 80% aqueous ethanol. A precipitate formed within 2 mins., which, after a few hrs., was filtered and recrystallized from an ethanol-acetone mixture, m.p. 177-179° (lit. val. (4), 180-181°), 1.4 g. (97.5%). IR (in nujol): 2260 (4.42), CN; 983 (10.17), cyclopropane ring (?). NMR spectrum (in acetone-$d_6$) showed two multiplets at $\tau$ 8.22 and $\tau$ 7.97.

Method II. One-half gram (5.10 mmoles) of cyclohexanone and 2.22 g. (15.3 mmoles) of bromomalononitrile were dissolved in 20 ml. of ethanol in a 50-ml. Erlenmeyer flask. The reaction mixture was kept overnight. The white precipitate that had formed was filtered and recrystallized from ethanol, m.p. 176-178°, 0.77 g. (71.9%).

11. 1,1,2,2-Tetracyano-4-methylspiro[2.5]octane

One gram (6.25 mmoles) of 2-methylcyclohexylidenemalononitrile and 1.5 g. (10.3 mmoles) of bromomalononitrile were dissolved in 30 ml. of ethanol. A precipitate formed in 16 hrs. The first crop was filtered after 24 hrs. and the second crop after standing for an additional 24 hrs. Recrystallization from ethanol yielded 0.55 g. (39.3%) of white crystals, m.p. 165-166°. IR (in nujol): 2275 (4.40), CN; 984 (10.16), cyclopropane ring (?). NMR (in acetone-$d_6$): $\tau$ 8.43 (d, J=6.5 c.p.s.), ring methyl; $\tau$ 8.22 (m), $C_5$, $C_6$, and $C_7$ methylene hydrogens; $\tau$ 7.93 (m), $C_8$ methylene hydrogens; $\tau$ 7.36 (m), methine hydrogen.

Anal. Calcd. for $C_{13}H_{12}N_4$: C, 69.62; H, 5.39; N, 24.98

Found: C, 69.73; H, 5.29; N, 25.10

12. 3,3-Nonamethylene-1,1,2,2-tetracyanocyclopropane

Crude cyclodecylidenemalononitrile (0.98 g., 4.85 mmoles) and bromomalononitrile (2.22 g., 15.3 mmoles) were dissolved in 12 ml. of ethanol. A precipitate formed in 15 mins., which, after standing for a few hrs., was filtered and recrystallized from an ethanol-acetone mixture, m.p. 214-216°, 0.45 g. (34.8%). IR (in nujol): 2280 (4.39), CN; 978 (10.23), cyclopropane ring (?). The NMR spectrum (in DMSO-$d_6$) showed two peaks at $\tau$ 8.43 and $\tau$ 8.03 in an area ratio of 10 : 7.94.

Anal. Calcd. for $C_{16}H_{18}N_4$: C, 72.15; H, 6.81; N, 21.04

Found: C, 72.14; H, 6.81; N, 21.11

13. 3,3-Undecamethylene-1,1,2,2-tetracyanocyclopropane

One-half gram (2.17 mmoles) of crude cyclododecylidenemalononitrile and 2 g. (13.8 mmoles) of bromomalononitrile were dissolved in 10 ml. of ethanol. A precipitate was formed in 1 hr., which, after standing for a few hours, was worked up as described in section 12, m.p. 197-200°, 0.6 g. (94%). IR (in nujol): 2265 (4.42), CN; 971 (10.30), cyclopropane ring (?). NMR spectrum (in acetone-d6) showed a large broad singlet at $\tau$ 8.53 and a multiplet at $\tau$ 8.09 in an area ratio of 14 : 8.02.

Anal. Calcd. for $C_{18}H_{22}N_4$: C, 73.44; H, 7.53; N, 19.03

Found: C, 73.59; H, 7.56; N, 19.12

14. 3,3-Tetradecamethylene-1,1,2,2-tetracyanocyclopropane

Crude cyclopentadecyclidenemalononitrile (obtained from 0.65 g. (2.89 mmoles) of cyclopentadecanone) and 2 g. (13.8 mmoles) of bromomalononitrile were dissolved in 15 ml. of ethanol in a 50-ml. Erlenmeyer flask. The solution was kept (at room temperature) for 6 days. Then 3 ml. of water was added to the flask. An oily residue formed at the bottom which gradually solidified upon scratching the flask wall. Filtration of the solid followed by recrystallization from ethanol yielded 0.35 g. (36% based on the amount of the ketone) of white crystals melting at 111-112°. IR (in nujol): 2280 (4.39), CN; 973 (10.28), cyclopropane ring (?). The NMR spectrum (in DMSO-$d_6$) showed a large peak at $\tau$ 8.64 and a smaller broad peak at $\tau$ 8.30 in an area ratio of 20 : 7.85.

Anal. Calcd. for $C_{21}H_{28}N_4$: C, 74.96; H, 8.39; N, 16.65

Found: C, 74.86; H, 8.38; N, 16.61

D. Preparation of 3-Alkyl-3-aryl-1,1,2,2-tetracyanocyclopropanes

1. 3-Methyl-3-phenyl-1,1,2,2-tetracyanocyclopropane

One gram (5.96 mmoles) of β-phenylethylidenemalononitrile and 1.45 g. (10.0 mmoles) of bromomalononitrile were dissolved in 40 ml. of ethanol. Crystals formed in 1.5 hr., which, after standing overnight, were filtered. To the filtrate was added an additional 1.45 g. of bromomalononitrile, and thereafter crystals were collected every 24 hrs. for 3 days. The last filtrate was added to 30 ml. of water with stirring and the resulting crystals were filtered. The combined crops, upon recrystallization from an ethanol-acetone mixture, gave 1.2 g. (86.6%) of crystals, m.p. 249-252° dec. (lit. val. (3), 225°). IR (in nujol): 2270 (4.41), CN; 988 (10.12), cyclopropane ring (?); 764 (13.09) and 700 (14.29), monosubstituted benzene ring. NMR spectrum (in acetone-$d_6$) showed a singlet for the ring methyl at τ 8.13 and a multiplet for the aromatic hydrogens, centered at τ 2.50.

2. 3-Methyl-3-m-chlorophenyl-1,1,2,2-tetracyanocyclopropane

One gram (4.93 mmoles) of β-m-chlorophenylethylidenemalononitrile and 1.5 g. (10.3 mmoles) of bromomalononitrile were dissolved in 50 ml. of ethanol. A precipitate formed in 2 hrs., which, after standing for an additional several hrs., was filtered and recrystallized from ethanol, m.p. 206-208°, 0.9 g. (68.1%). IR (in nujol): 2266 (4.41), CN; 988 (10.12), cyclopropane ring (?); 794 (12.59) and 905 (11.05), 1,3-disubstituted benzene. NMR spectrum (in acetone-$d_6$) showed a singlet for the cyclopropyl methyl at τ 7.93 and three multiplets for the aromatic hydrogens at τ 2.42, τ 2.05, and τ 1.75.

Anal. Calcd. for $C_{14}H_7ClN_4$: C, 63.05; H, 2.65; Cl, 13.30; N, 21.01

Found: C, 62.26; H, 2.81; Cl, 13.57; N, 20.77

3. 3-Methyl-3-p-methylphenyl-1,1,2,2-tetracyanocyclopropane

One gram (5.49 mmoles) of β-p-methylphenylethylidenemalononitrile and 1.45 g. (10.0 mmoles) of bromomalononitrile were dissolved in 50 ml. of ethanol. A precipitate formed in 15 hrs., which, after standing for an additional 3 hrs., was filtered. To the filtrate was added 0.9 g. of bromomalononitrile and the second crop was collected after standing overnight. The combined product, upon recrystallization from ethanol, gave 1.1 g. (81.2%) of white crystals, m.p. 222-224°. IR (in nujol): 2262 (4.42), CN; 985 (10.15), cyclopropane ring (?); 817 (12.24), 1,4-disubstituted benzene. NMR (in acetone-$d_6$): $\tau$ 7.98 (s), cyclopropyl methyl; $\tau$ 7.62 (s), phenyl methyl; $\tau$ 2.65 (d) and $\tau$ 2.18 (d) in an $A_2B_2$ pattern, aromatic hydrogens.

Anal. Calcd. for $C_{15}H_{10}N_4$: C, 73.16; H, 4.09; N, 22.75

Found: C, 73.18; H, 4.03 N, 22.62

4. 3-Methyl-3-p-methoxyphenyl-1,1,2,2-tetracyanocyclopropane

One gram (5.04 mmoles) of β-p-methoxyphenylethylidenemalononitrile and 2.18 g. (15.0 mmoles) were dissolved in 50 ml. of ethanol. Crystals formed in 20 hrs., which, after standing for an additional 24 hrs., were filtered. To the filtrate was added an additional 2 g. of bromomalononitrile and, after 24 hrs., the second crop was collected. The combined product, on recrystallization from ethanol, gave 0.46 g. (51.2% based on the amount of the reacted β-p-methoxyphenylethylidenemalononitrile) of white crystals, m.p. 215-217°. IR (in nujol): 2300 (4.35), CN; 990 (10.10), cyclopropane ring (?); 849 (11.78), 1,4-disubstituted benzene. NMR (in acetone-$d_6$):

7.98 (s), cyclopropyl methyl; 6.15 (s), methoxyl methyl; 2.93 (d) and 2.14 (d) in an $A_2B_2$ pattern, aromatic hydrogens.

Anal. Calcd. for $C_{15}H_{10}N_4O$: C, 68.69; H, 3.84; N, 21.36

Found: C, 68.52; H, 3.78; N, 21.38

Removal of solvent (using a rotary evaporator) from the final filtrate resulted in a solid residue, which, on recrystallization from ethanol, gave 0.32 g. (1.61 mmoles) of unchanged β-p-methoxyphenylethylidenemalononitrile.

5. 3-Methyl-3-β-naphthyl-1,1,2,2-tetracyanocyclopropane

One gram (4.58 mmoles) of β-2-naphthylethylidenemalononitrile and 2.18 g. (15.0 mmoles) of bromomalononitrile were dissolved in 50 ml. of ethanol. The precipitate that had formed in 1 hr., was filtered after standing for 24 hrs., and upon recrystallization from an ethanol-acetone mixture, yielded 0.53 g. (54.8% based on the amount of the reacted β-2-naphthylethylidenemalononitrile) of white crystals, m.p. 255-260°. IR (in nujol): 2280 (4.38), CN; 985 (10.15), cyclopropane ring (?); 870 (11.49), 816 (12.25), and 749 (13.35), β-naphthyl ring. NMR (in acetone-$d_6$): τ 7.84 (s), cyclopropyl methyl; τ 2.37 (m), τ 2.02 (m), and τ 1.43 (s), aromatic hydrogens.

Anal. Calcd. for $C_{18}H_{10}N_4$: C, 76.58; H, 3.57; N, 19.85

Found: C, 75.03; H, 3.54; N, 19.50

Removal of solvent from the filtrate followed by recrystallization (from ethanol) of the resulting residue gave 0.25 g. (1.15 mmole) of recovered β-2-naphthylethylidenemalononitrile.

6. 3-Ethyl-3-phenyl-1,1,2,2-tetracyanocyclopropane

β-Phenylpropylidenemalononitrile (0.91 g., 5.0 mmoles) and bromomalononitrile (1.20 g., 8.0 mmoles) were dissolved in 20 ml. of ethanol and allowed

to stand for a few days. The reaction mixture was then poured into a 50-ml. beaker and cooled in an ice bath. Crystals that had formed were filtered and recrystallized from ethanol, m.p. 225-227°. 0.22 g. (17.8%). IR (in nujol); 2275 (4.40), CN; 990 (10.10), cyclopropane ring (?); 774 (12.94) and 702 (14.25), the monosubstituted benzene. NMR (in acetone-$d_6$): $\tau$ 8.89 (t), $CH_3CH_2$; $\tau$ 7.68 (q), $CH_3CH_2$; $\tau$ 2.21 (m), aromatic hydrogens. Area ratio: 3.08 : 2.18 : 5.00.

Anal. Calcd. for $C_{15}H_{10}N_4$: C, 73.16; H, 4.09; N, 22.75

Found: C, 73.08; H, 4.11; N, 22.68

7. Spiro [2,2,3,3-tetracyanocyclopropane-1,1'-tetralin]

Six-tenths (3.1 mmoles) of 2,3-benzocyclohexylidenemalononitrile was placed in a 50-ml. Erlenmeyer flask containing 30 ml. of ethanol and 5 ml. of water. The flask was gently warmed on a hot plate until a complete solution was obtained and then the solution was allowed to cool to room temperature. One and one-half gram (10.3 mmoles) of bromomalononitrile was dissolved in this solution. Crystals that had formed in 6-7 hrs. were filtered after 12 hrs. To the filtrate was added 2 ml. of water and the second crop was collected after standing for an additional several hrs. The combined product was recrystallized from ethanol, m.p. 167-170., 0.29 g. (54.2% based on the amount of the reacted 2,3-benzocyclohexylidenemalononitrile). IR (in nujol); 2265 (4.41), CN; 968 (10.33), cyclopropane ring (?); 743 (13.46), benzene ring.

Anal. Calcd. for $C_{16}H_{10}N_4$: C, 74.40; H, 3.90; N, 21.69

Found: C, 74.31; H, 3.98; N, 21.53

The final filtrate, after removal of solvent followed by recrystallization of the resulting solid, gave 0.2 g. (1.3 mmoles) of unchanged 2,3-benzocyclohexylidenemalononitrile.

It seemed very important to use a solvent made up of ethanol and water according to the above proportion and to run the reaction at room temperature. An elevated reaction temperature or use of solvent richer in ethanol (90% aqueous ethanol, for example) was found to cause formation of brominated compound described on page 98.

8. 3-Methyl-3-$\alpha$-thienyl-1,1,2,2-tetracyanocyclopropane

One gram (5.7 mmoles) of $\beta$-2-thienylethylidenemalononitrile and 1g. (6.9 mmoles) of bromomalononitrile were dissolved in 50 ml. of ethanol and gently warmed on a steam bath for several mins. Precipitate that had formed in 30 mins. was filtered and recrystallized from ethanol, m.p. 207-210° dec., 0.3 g. (22.1%). IR (in nujol): 2275 (4.40), CN; 985 (10.15), cyclopropane ring (?); 717 (13.98), thiophene ring. NMR (in DMSO-$d_6$): $\tau$ 8.16 (s), cyclopropyl methyl; $\tau$ 2.87 (m) and $\tau$ 2.25 (m), aromatic hydrogens.

Anal. Calcd. for $C_{12}H_6N_4S$: C, 60.49; H, 2.54; N, 23.52; S, 13.46

Found: C, 60.47; H, 2.76; N, 23.52; S, 13.31

E. Preparation of Some Dimers of Alkylidenemalononitriles

1. Isopropylidenemalononitrile Dimer

Method I. When isopropylidenemalononitrile was allowed to stand at room temperature for a long time (6-10 months), a precipitate formed at the bottom of the container. Recrystallization of this precipitate from ethanol

gave pale yellow crystals of isopropylidenemalononitrile dimer, m.p. 171-174° (lit. val. (64) 168-170°). IR (in nujol): 3440 (2.91), 3340 (2.99), 3230 (3.10), NH; 2215 (4.51), CN; 1465 (6.08), 1614 (6.20), 1578 (6.34), C=C and/or C=N. UV (in ethanol): 218.5 (11,540), 240.0 (5,687) (sh.), 310.0 (5,770). NMR (in DMSO-$d_6$); $\tau$ 8.74 (d), gem. dimethyls; $\tau$ 8.15 (d., J=1.7 c.p.s.), allylic methyl; $\tau$ 4.88 (q., J=1.6 c.p.s.); $\tau$ 2.37 (s), $NH_2$: Area ratio was 6 : 2.62 : 0.75 : 1.69 in the order described.

The condensation reaction of acetone and malononitrile gives a small amount of isopropylidenemalononitrile dimer as well as the monomer. Usually the dimer is obtained by recrystallizing the solid residue remaining in the bottom of the distillation flask after the monomer has been distilled out.

Method II. One gram (9.43 mmoles) of isopropylidenemalononitrile was dissolved in 7 ml. of ethanol contained in a 50-ml. Erlenmeyer flask. To this solution was added 5 drops of piperidine. The mixture was kept at room temperature for 1.5 hr. Then the contents in the flask were poured into 20 ml. of water contained in a 50-ml. beaker. A precipitate formed immediately. After one-half hr., crystals were filtered and recrystallized from ethanol, m.p. 168-171°, 0.75 g. (75%). The m.m.p. with the compound prepared by Method I did not depress.

2. 2-Butylidenemalononitrile Dimer

Method I. In a 100-ml. round-bottomed flask fitted with a Barrett distilling receiver and a water condenser, were placed 14.4 g. (0.2 mole) of 2-butanone, 13.2 g. (0.2 mole) of malononitrile, 3 g. of ammonium acetate, 6 ml. of glacial acetic acid, and 30 ml. of benzene. The mixture was

refluxed for 4 hrs. Then reflux was discontinued and the reaction mixture was allowed to cool to room temperature. An additional 20 ml. of benzene was added to the flask and the entire reaction mixture was washed with three 50-ml. portions of water. The organic layer was dried over 20 g. of anhydrous sodium sulfate for several hrs. The drying agent was removed by filtration and the solvent was stripped with the aid of a water aspirator. Further fractionation gave 9.00 g. (37.5%) of pale yellow liquid of 2-butylidenemalononitrile, $b_4$ 82° (lit. val. (65) $b_8$ 102°), $n_D^{19}$ 1.4707.

After the 2-butylidenemalononitrile was fractionated, there was formed a gummy residue in the distillation flask. This was purified by twice recrystallizing it from ethanol. There was obtained 2.70 g. (11.2%) of 2-butylidenemalononitrile dimer, m.p. 159-164° (lit. val. (44) 167-169°). IR (in nujol): 3430 (2.98), 3360 (2.98), 3260 (3.07), NH; 2220 (4.50), CN; 1652 (6.05), 1593 (6.28), C=C and/or C=N. UV (in ethanol): 301 (15,020), 243 (9,661), 217 (6,248), 213 (sh). NMR (in DMSO-$d_6$): $\tau$ 9.07 (t), $CH_2\underline{CH_3}$; $\tau$ 8.43 (q), $\underline{CH_2}CH_3$; $\tau$ 8.80 (s), ring methyl; $\tau$ 8.27 (d), allylic methyl; $\tau$ 7.66 (s), ring methylene hydrogens; $\tau$ 4.44 (q., J=7.0 c.p.s.), olefinic hydrogen; $\tau$ 2.93 (s), $\underline{NH_2}$. Area ratio: $\tau$ 9.07-8.27 : $\tau$ 7.66 : $\tau$ 4.44 : $\tau$ 2.93 = 11 : 1.93 : 0.76 : 1.75.

Anal. Calcd. for $C_{14}H_{16}N_4$: C, 69.97; H, 6.71; N, 23.32

Found: C, 70.01; H, 6.74; N, 23.25

Method II. In a 50-ml. Erlenmeyer flask were placed 2 g. (16.6 mmoles) of 2-butylidenemalononitrile and 10 ml. of ethanol. While stirring the solution using a magnetic stirrer, 10 drops of piperidine was added to the reaction mixture. After 1.5 hr., the stirring was discontinued and the

contents in the flask was treated in the same manner described in Method II of preparation of isopropylidenemalononitrile dimer. Recrystallization from ethanol yielded 1.35 g. (67.5%) of light yellow crystals melting at 158-162°. The m.m.p. with the compound prepared by Method I did not depress.

3. Cyclopentylidenemalononitrile Dimer

Method I. Cyclopentanone (20 g., 0.230 mole), 14.8 g. (0.224 mole) of malononitrile, 3.0 g. of ammonium acetate, 6.0 ml. of glacial acetic acid, and 30 ml. of benzene were treated in the manner described in Method I for preparation of 2-butylidenemalononitrile dimer. While cyclopentylidene-malononitrile was distilled, there began to form a precipitate in the flask*. Distillation was discontinued and the contents of the flask were transferred to a 100-ml. beaker. The beaker was kept at room temperature until crystallization of the reaction mixture appeared to be completed (about an hr.). Filtration followed by recrystallization from ethanol yielded 11.72 g. (39.2%) of lemon yellow crystals, m.p. 187-190°. IR (in nujol): 3440 (2.91), 3370 (2.97), 3260 (3.07), NH; 2240 (4.46), CN; 1650 (6.06), 1589 (6.29), C=C and/or C=N. UV (in ethanol): 308 (12,226), 241 (8,681), 224 (6,639), 215 (sh.). NMR (in DMSO-$d_6$): $\tau$ 2.72 (s), $\underline{NH_2}$ $\tau$ 4.52 (d, J=1.8 c.p.s.), olefinic hydrogen; $\tau$ 8.23 (m), $\tau$ 7.61 (m), $\tau$ 6.97 (m),

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* No cyclopentylidenemalononitrile monomer was obtained in this particular experiment. However, in one of previous experiments, the monomer was obtained in a yield of 22.1%, $b_4$ 113-114°, $n_D^{23}$ 1.4995. IR (in $CCl_4$): 2250 (4.44), CN; 1618 (6.18), C=C. UV (in ethanol): 238 (10,885). The NMR spectrum (neat) showed two multiplets at $\tau$ 8.11 ($C_3$- and $C_4$-hydrogens) and $\tau$ 7.24 ($C_2$- and $C_5$-hydrogens) in an area ratio of 3.88 : 4. The residue obtained in this latter case was a tar which could not be identified.

rest of hydrogens in the molecule. Area ratio: $\tau$ 2.72 : $\tau$ 4.52 : $\tau$ 6.97 - 8.23 = 1.89 : 0.97 : 13.

Anal. Calcd. for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20

Found: C, 72.82; H, 6.03; N, 21.30

Method II. Four and six-tenths grams (0.057 mole) of cyclopentanone, 3.30 g. (0.050 mole) of malononitrile, 0.5 g. of ammonium acetate, 1.0 ml. of glacial acetic acid, and 10 ml. of benzene were treated in the manner described in Method I to obtain a dry benzene solution of the cyclopentylidenemalononitrile monomer (25 ml.). The benzene solution was placed in a 250-ml. Erlenmeyer flask and 0.6 ml. of piperidine and 30 ml. of water were added. The solution was stirred using magnetic stirrer for 1 hr. A precipitate formed. After a few hrs., the precipitate was filtered and recrystallized from ethanol, m.p. 187-189.5°, 4.06 g. (58.5%). The m.m.p. with the compound prepared by Method I did not depress.

F. Preparation of 3-Aryl-1,1,2,2-tetracyanocyclopropanes

An ethanolic solution of arylidenemalononitrile was mixed with an ethanolic solution of equimolar or excess (twice or less) amount of bromomalononitrile. A precipitate formed in sometime between a few mins. and a few hrs. depending on the aryl group. The reaction mixture was allowed to stand for several hrs. after the first precipitate appeared. Then the precipitate was filtered and purified by recrystallizing from ethanol or more often from an ethanol-acetone mixture. Compounds thus prepared are presented in Table 4 and some of their NMR spectral data appear in Table 5 (page 26 and 29, respectively).

A typical preparation follows: To 1 g. (6.5 mmoles) of benzylidenemalononitrile dissolved in 10 ml. of ethanol contained in a 50-ml. Erlenmeyer flask was added 1.16 g. (8.0 mmoles) of bromomalononitrile dissolved in 10 ml. of ethanol. A precipitate formed within a few mins. After 5 hrs, the precipitate was filtered. Recrystallization from an ethanol-acetone mixture yielded 1.35 g. (91.7%) of crystals, m.p. 227-230° dec.

G. Preparation of 3,3-Dialkyl-2-carbethoxy-1,1,2-tricyanocyclopropanes

1. 3,3-Dimethyl-2-carbethoxy-1,1,2-tricyanocyclopropane

Method I. One-half gram (3.26 mmoles) of ethyl isopropylidenecyanoacetate and 1.0 g. (6.90 mmoles) of bromomalononitrile were dissolved in 12 ml. of 85% aqueous ethanol contained in a 50-ml. Erlenmeyer flask. The solution was kept at room temperature for 1 hr., when the precipitate started forming. The reaction mixture was allowed to stand for an additional few hrs. Then the precipitate was filtered. Recrystallization from ethanol gave 0.52 g. (73.5%) of white crystals, m.p. 141-143° (lit. val. (14) 135°). IR (in nujol): 2270 (4.41), CN; 1747 (5.72), CO; 1280 (7.81), 1248 (8.01), C-O-C; 980 (10.20), cyclopropane ring (?). The NMR spectrum (in acetone-$d_6$) showed $COOC_2H_5$ at $\tau$ 8.62 (t) and $\tau$ 5.62 (q) and two ring methyls at $\tau$ 8.31 (s, cis to $COOC_2H_5$) and $\tau$ 8.21 (s, trans to $COOC_2H_5$).

When the reaction mixture was warmed on a steam bath, the product formed in 10 mins.

Method II. Two grams (18.9 mmoles) of isopropylidenemalononitrile and 3.84 g. (20 mmoles) of ethyl bromocyanoacetate were dissolved in 25 ml. of 50% aqueous ethanol. The mixture was allowed to stand at room temperature.

Crystals formed after 5 hrs. The product was filtered after 24 hrs. Recrystallization from an ethanol-acetone mixture yielded 1.17 g. (28.6%) of white crystals, m.p. 137-139°. The m.m.p. with the compound prepared by Method I did not depress.

2. 3-Methyl-3-ethyl-2-carbethoxy-1,1,2-tricyanocyclopropane

One gram (5.98 mmoles) of ethyl 2-butylidenecyanoacetate and 1.01 g. (7.00 mmoles) of bromomalononitrile were dissolved in 12 ml. of 80% aqueous ethanol contained in a 50-ml. Erlenmeyer flask and kept at room temperature for about 20 hrs. The contents of the flask were transferred to a 50-ml. round-bottomed flask. Two millilitres of water was added and the mixture was refluxed for a few hrs. The contents were then poured into a 50-ml. beaker and cooled in an ice bath until a precipitate formed. Filtration followed by recrystallization from ethanol yielded 0.88 g. (63.7%) of white crystals, m.p. 87-89° (lit. val. (14) 89°). IR (in nujol): 2260 (4.42), CN; 1745 (5.73), CO; 1275 (7.84), C-O-C; 978 (10.23), cyclopropane ring (?). NMR (in acetone-$d_6$): $\tau$ 8.80 (m, 4 triplets), $CH_2\underline{CH_3}$ and $COOCH_2\underline{CH_3}$; $\tau$ 8.39 (s) and $\tau$ 8.26 (s), ring methyl cis and trans, respectively, to $COOCH_2CH_3$; $\tau$ 7.94 (m), $\underline{CH_2}CH_3$; $\tau$ 5.64 (q, 2 quartets when expanded), $COO\underline{CH_2}CH_3$. An attempt to prepare this compound from 2-butylidenemalononitrile and ethyl bromocyanoacetate was unsuccessful.

3. 3-Methyl-3-n-propyl-2-carbethoxy-1,1,2-tricyanocyclopropane

One gram (5.52 mmoles) of ethyl 2-pentylidenecyanoacetate and 1.02 g. (7.04 mmoles) of bromomalononitrile were mixed in 50% aqueous ethanol in 50-ml. Erlenmeyer flask and warmed on a steam bath for several mins. The dark brown reaction mixture was kept at room temperature for about a month.

After this time, the solvent was removed with aid of a rotary evaporator. To the concentrated residue thus obtained was added 10 ml. of water and the mixture was cooled in an ice bath for half an hr. A precipitate was obtained and recrystallized from ethanol, m.p. 63-65°, 0.5 g. (37%). IR (in nujol): 2260 (4.42), CN; 1747 (5.72), CO; 1269 (7.88), C-O-C; 979 (10.21) cyclopropane ring (?). NMR (in acetone-$d_6$): $\tau$ 8.98 (t), $CH_2CH_2C\underline{H}_3$; $\tau$ 8.38 (s) and $\tau$ 8.25 (s), ring methyl cis and trans, respectively, to $COOC_2H_5$; $\tau$ 8.64 (t) and $\tau$ 5.62 (q), $COOC_2\underline{H}_5$. The methylene hydrogens in the n-propyl group appeared in a multiplet above $\tau$ 8.03.

Anal. Calcd. for $C_{13}H_{15}N_3O_2$: C, 63.66; H, 6.16; N, 17.13

Found: C, 63.63; H, 6.05; N, 17.31

An attempt to prepare this compound from 2-pentylidenemalononitrile and ethyl bromocyanoacetate was not successful.

4. 3-Methyl-3-isopropyl-2-carbethoxy-1,1,2-tricyanocyclopropane

Ethyl 3-methyl-2-butylidenecyanoacetate (2.18 g., 12 mmoles) and bromomalononitrile (2.18 g., 15 mmoles) were dissolved in 20 ml. of aqueous ethanol (about 80%) contained in a 100-ml. round-bottomed flask. The mixture was refluxed for 5 hrs. and then set aside at room temperature for 2 weeks. Work-up of the reaction mixture yielded 0.19 g. (6.46%) of crystals, m.p. 131-134° (from ethanol). IR (in nujol): 2275 (4.40), CN; 1745 (5.73), CO; 1256 (7.96), C-O-C; 1017 (9.83), cyclopropane ring (?). NMR (in acetone-$d_6$): $\tau$ 8.99 (d) and $\tau$ 8.79 (d), $CH(C\underline{H}_3)_2$; $\tau$ 8.65 (t) and $\tau$ 5.62 (q), $COOC_2\underline{H}_5$; $\tau$ 8.35 (s), ring methyl; $\tau$ 7.76 (m), $C\underline{H}(CH_3)_2$.

Anal. Calcd. for $C_{13}H_{15}N_3O_2$: C, 63.66, H, 6.16; N, 17.13

Found: C, 63.14; H, 6.01; N, 17.31

An attempt to prepare this compound from 3-methyl-2-butylidenemalononitrile and ethyl bromocyanoacetate was not successful.

5. 3,3-Diethyl-2-carbethoxy-1,1,2-tricyanocyclopropane

Two grams (11 mmoles) of ethyl 3-pentylidenecyanoacetate and 2.2 g. (15 mmoles) of bromomalononitrile were dissolved in 30 ml. of ethanol in a 100-ml. round-bottomed flask. The mixture was set aside at room temperature for 2 days and then refluxed for several hrs. Then the contents were cooled to room temperature. The reaction mixture was poured into a 100-ml. beaker and further cooled in an ice bath. Crystals that formed were filtered and recrystallized from ethanol, m.p. 93-95°, 0.95 g. (35.2%). IR (in nujol): 2255 (4.43), CN; 1741 (5.74), CO; 1272 (7.86), C-O-C; 975 (10.26), cyclopropane ring (?). NMR spectrum (in acetone-$d_6$) showed three triplets at $\tau$ 8.93, $\tau$ 8.80 and $\tau$ 8.63 and three quartets at $\tau$ 8.00, $\tau$ 7.97 and $\tau$ 5.62 with an area ratio of triplets vs. quartets being 6.00 : 4.22.

Anal. Calcd. for $C_{13}H_{15}N_3O_2$: C, 63.66, H, 6.16; N, 17.13

Found: C, 63.35; H, 6.09; N, 17.04

An attempt to prepare this compound from 3-pentylidenemalononitrile and ethyl bromocyanoacetate was not successful

6. 3,3-Tetramethylene-2-carbethoxy-1,1,2-tricyanocyclopropane

One and eight-tenths gram (10 mmoles) of ethyl cyclopentylidenecyanoacetate and 1.9 g. (13 mmoles) of bromomalononitrile were dissolved in 15 ml. of ethanol contained in a 50-ml. Erlenmeyer flask and kept at room temperature. After a few hrs., 2 ml. of water was added to the flask, when there was formed a brown oily layer at the bottom of the flask. After 2 days, the oil solidified. Recrystallization of the solid mass from ethanol

yielded 0.35 g. (14.5%) of needles (pale gray), m.p. 136-139°. IR (in nujol): 2260 (4.42), CN; 1743 (5.74), CO; 1282 (7.80), C-O-C; 970 (10.34), cyclopropane ring (?). NMR spectrum (in DMSO-$d_6$) showed the $COOC_2\underline{H}_5$ at $\tau$ 8.66 (t) and $\tau$ 5.72 (q) and the ring hydrogens at $\tau$ 8.02 (m, consisted of 3 main peaks).

Anal. Calcd. for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.28

Found C, 64.16; H, 5.31; N, 17.35

An attempt to prepare this compound from cyclopentylidenemalononitrile and ethyl bromocyanoacetate was not successful.

7. 3,3-Pentamethylene-2-carbethoxy-1,1,2-tricyanocyclopropane

Method I. One-half gram (2.59 mmoles) of ethyl cyclohexylidenecyanoacetate, 0.75 g. (5.00 mmoles) of bromomalononitrile, and 10 ml. of 80% aqueous ethanol were placed in a 50-ml. Erlenmeyer flask. The flask was gently shaken until the solution was completed and kept at room temperature. One hr. later, a precipitate appeared. After 4 hrs., the precipitate was filtered and recrystallized from ethanol, m.p. 129-131°, 0.65 g. (97.5%). IR (in nujol): 2275 (4.40), CN; 1745 (5.73), CO; 1274 (7.85), C-O-C; 981 (10.19), cyclopropane ring (?). NMR spectrum (in acetone-$d_6$) showed ethyl hydrogens at $\tau$ 8.64 (t) and $\tau$ 5.61 (q) and the ring hydrogens at $\tau$ 8.33 (m) and $\tau$ 7.96 (m).

Anal. Calcd. for $C_{14}H_{15}N_3O_2$: C, 65.35; H, 5.88; N, 16.33

Found: C, 65.30; H, 5.80; N, 16.38

Method II. In a 50-ml. round-bottomed flask were placed 1 g. (6.85 mmoles) of cyclohexylidenemalononitrile, 1.54 g. (8.0 mmoles) of ethyl bromocyanoacetate, and 15 ml. of 50% aqueous ethanol and the mixture was

refluxed overnight. Reflux was discontinued and the reaction mixture was kept at room temperature for a few hrs. During this time a precipitate formed in the flask. Filtration followed by recrystallization from ethanol gave 0.42 g. (23.8%) of white crystals, m.p. 131-133°. The m.m.p. with the compound prepared by Method I did not depress.

H. Preparation of 3-Aryl-2-carbethoxy-1,1,2-tricyanocyclopropanes

1. 3-Phenyl-2-carbethoxy-1,1,2-tricyanocyclopropane

Method I. One gram (4.98 mmoles) of ethyl benzylidenecyanoacetate and 0.74 g. (5.1 mmoles) of bromomalononitrile were dissolved in 20 ml. of 50% aqueous ethanol. The mixture was refluxed for several hrs., during which time a precipitate formed in the flask. Filtration followed by recrystallization from ethanol yielded 1.0 g. (76.7%) of white crystals, m.p. 124.5-126°. IR (in nujol): 2260 (4.43), CN; 1734 (5.77), CO; 1288 (7.81), 1233 (8.11), C-O-C; 740 (13.51), 700 (14.28), monosubstituted benzene; 1015 (9.85), cyclopropane ring (?). NMR (in acetone): $\tau$ 8.61 (t) and $\tau$ 5.61 (q), $COOC_2\underline{H}_5$; $\tau$ 5.74 (s), H, cyclopropyl; $\tau$ 2.52 (m), H, aromatic.

Anal. Calcd. for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84

Found: C, 67.82; H, 4.11; N, 16.00

Method II. One gram (6.5 mmoles) of benzylidenemalononitrile and 1.25 g. (6.8 mmoles) of ethyl bromocyanoacetate were placed in a 50-ml. round-bottomed flask containing 27 ml. of 60% aqueous ethanol. The contents in the flask were refluxed for 3 hrs. An oily layer which formed at the bottom of the container solidified on being kept in a refrigerator for a

few hrs. The solid mass was filtered and recrystallized from ethanol, 0.5 g. (29%), m.p. 123-125°. The m.m.p. with the compound prepared by Method I did not depress.

2. 3-p-Methoxyphenyl-2-carbethoxy-1,1,2-tricyanocyclopropane

Method I. In a 125-ml. Erlenmeyer flask were placed 1.16 g. (5 mmoles) of ethyl anisylidenecyanoacetate, 1.5 g. (10.3 mmoles) of bromomalononitrile, and 10 ml. of ethanol. The mixture was shaken until a complete solution was obtained, then kept overnight at room temperature. The precipitate that had formed was filtered and treated with Norit A. Recrystallization from ethanol gave 0.53 g. (36.2%) of crystals, m.p. 95-97°. IR (in nujol): 2275 (4.40), CN; 1743 (5.74), CO; 1267 (7.89), 1180 (8.47), C-O-C; 990 (10.10), cyclopropane ring (?); 820 (12.19), 1,4-disubstituted benzene. NMR (in acetone): $\tau$ 8.63 (t) and $\tau$ 5.58 (q), $COOC_2\underline{H}_5$; $\tau$ 6.19 (s), $C\underline{H}_3O$; $\tau$ 5.79 (s), H, cyclopropyl; $\tau$ 3.00 (d) and $\tau$ 2.40 (d) ($A_2B_2$), H, aromatic.

Anal. Calcd. for $C_{16}H_{13}N_3O_3$: C, 65.08; H, 4.44; N, 14.23

Found: C, 64.74; H, 4.35; N, 14.29

Method II. In a 50-ml. Erlenmeyer flask were placed 0.92 g. (5 mmoles) of anisylidenemalononitrile, 2.00 g. (10 mmoles) of ethyl bromocyanoacetate, and 30 ml. of ethanol. The mixture was shaken until a complete solution was obtained and set at room temperature for 2 days, after which time crystals started forming. After a week, the crystals were filtered and recrystallized from ethanol, m.p. 105-106°, 0.89 g. (60.3%). The m.m.p. with the compound prepared by Method I did not depress.

I. Preparation of 2-carboxamido-1,1,2-tricyanocyclopropanes

1. 3,3-Pentamethylene-2-carboxamido-1,1,2-tricyanocyclopropane

In a 50-ml. Erlenmeyer flask was placed 1.6 g. (10 mmoles) of cyclohexylidenecyanoacetamide, 4.35 g. (30 mmoles) of bromomalononitrile, and 25 ml. of 80% aqueous ethanol. The flask was shaken until solution was completed and kept at room temperature for 2 days. Then the contents in the flask were transferred into a 100-ml. beaker and 20 ml. of water was added. The beaker was placed in an ice bath for a few hrs. (3-4 hrs.). The precipitate which had formed during this time period was filtered and washed with water. Recrystallization from ethanol gave 0.15 g. (7.15% based on 10 mmoles of cyclohexylidenecyanoacetamide) of 3,3-pentamethylene-1,1,2,2-tetracyanocyclopropane, m.p. 176-178°.

The filtrate was further kept in an ice bath for several hrs. (6-7 hrs.) occasionally scratching the wall of the beaker. The precipitate that formed was filtered and recrystallized by dissolving in a minimum amount of ethanol at room temperature and then filtering followed by cooling in an ice bath. The crystals thus obtained were crude, beginning to melt at 140° and finally decomposing at 180°, 1.40 g. (61.3%). IR (in nujol): 3430 (2.91), 3360 (2.98), 3200 (3.13), NH; 1700 (5.88), CO: 1615 (6.19), amide II band; 970 (10.31), cyclopropane ring (?). NMR spectrum (in acetone-$d_6$) showed the cyclohexane ring hydrogens in 2 multiplets at $\tau$ 8.27 and $\tau$ 8.07 and the amide hydrogens in 2 broad peaks at $\tau$ 2.58 and $\tau$ 2.02 in an area ratio of 10 : 1.73. This compound could not be recrystallized in the ordinary manner without undergoing a chemical change.

2. 3-Phenyl-2-carboxamido-1,1,2-tricyanocyclopropane

One and seven-tenths gram (10 mmoles) of benzylidenecyanoacetamide was dissolved in 50 ml. of ethanol contained in a 125-ml. Erlenmeyer flask. To this solution was added 3 g. (20 mmoles) of bromomalononitrile and the flask was shaken until the solution was completed. The solution was kept at room temperature. Within one-half hr., a precipitate appeared. After a few (3-4) hrs., the first crop of 1.75 g. was collected. After overnight the second crop of 0.35 g. was collected, 2.1 g. (89%). Crude crystals decomposed sharply at 185° (m.p. for this compound was taken by heating the apparatus at a rate of 20-30°/min.). IR (in nujol): 3500 (2.86), 3300 (3.03), 3200 (3.13), NH; 2270 (4.41), CN; 1710 (5.85), 1687 (5.93), CO; 1605 (6.23), amide II band; 740 (13.51), 700 (14.29), monosubstituted benzene. NMR (in DMSO-$d_6$): $\tau$ 5.63 (s), H, cyclopropyl; $\tau$ 2.37 (m), H, aromatic; $\tau$ 1.47, $CONH_2$. This compound could not be recrystallized in the ordinary manner without undergoing a chemical change.

3. 3-p-Chlorophenyl-2-carboxamido-1,1,2-tricyanocyclopropane

One and nine-tenths gram (9.18 mmoles) of p-chlorobenzylidenecyanoacetamide was dissolved in 250 ml. of warm (40-45°) ethanol contained in a 500-ml. Erlenmeyer flask. To this solution was added 3 g. (20 mmoles) of bromomalononitrile and the mixture was shaken until solution was nearly complete. The resultant solution was filtered to remove undissolved impurities and allowed to stand at room temperature for 3 hrs. Then ethanol was evaporated using a rotary evaporator below 40° until the residual volume decreased to about 70 ml. The residue was transferred

into a 100-ml. beaker and cooled in an ice bath. Crystals that formed were filtered and washed thoroughly with water. The filtrate was further evaporated and treated in the same manner to obtain the second crop. White crystalline product that had not been recrystallized (this compound could not be recrystallized in the ordinary manner without undergoing a chemical change) sharply decomposed at 202° (m.p. measured at a heating rate of 20-30°/min.), 2.2 g. (88.5%). IR (in nujol): 3435 (2.91), 3365 (2.97), 3295 (3.03), 3225 (3.10), NH; 2280 (4.38), CN: 1704 (5.87), 1684 (5.94), CO; 1603 (6.24), amide II band; 812 (12.31), 1,4-disubstituted benzene. NMR (in DMSO-$d_6$): $\tau$ 5.42 (s), H, cyclopropyl; $\tau$ 2.50 (d) and $\tau$ 2.33 (d) ($A_2B_2$), H, aromatic; $\tau$ 1.48 (s, broad), $CONH_2$.

Anal. Calcd. for $C_{13}H_7ClN_4O$: C, 57.68; H, 2.61

Found: C, 57.71; H, 2.77

J. Preparation of 1,5-Dicyano-2-imino-3-aza-4-ketobicyclo[3.1.0]hexanes

1. 1,5-Dicyano-2-imino-3-aza-4-keto-6,6-pentamethylenebicyclo[3.1.0] hexane

One-half gram (2.19 mmoles) of 3,3-pentamethylene-2-carboxamido-1,1,2-tricyanocyclopropane was dissolved in a few (3-4) ml. of boiling methanol. When the solution was completed, 1 ml. of water was added and the resultant aqueous solution was further heated on a hot plate for a min. The solution was filtered and then cooled in an ice bath. Crystals thus obtained were recrystallized from ethanol, m.p. 225-228° dec., 0.47 g. (94%). IR (in nujol): 3380 (2.96), NH; 2260 (4.42), CN; 1737 (5.76), CO; 1652 (6.05), 1567 (6.38), (both strong and broad), C=N and/or NH; 1007 (9.93), cyclo-

propane ring (?). NMR spectrum taken in a dimethyl sulfoxide-$d_6$ solution at a probe temperature of about 100° showed the cyclohexane ring hydrogens in a large peak at $\tau$ 8.38 and a small adjoining peak at $\tau$ 8.10. The imino and amido hydrogens appeared in a weak broad peak at $\tau$ 1.22 (the chemical shift of this peak was found to increase, the longer the sample was kept in the probe). Area ratio: ring hydrogens : N-hydrogens, 10 : 1.8. A half drop of ordinary dimethyl sulfoxide ($\tau$ 7.38) was used as an internal reference.

Anal. Calcd. for $C_{12}H_{12}N_4O$: C, 63.14; H, 5.30; N, 24.55

Found: C, 63.23; H, 5.23; N, 24.51

2. 1,5-Dicyano-2-imino-3-aza-4-keto-6-phenylbicyclo[3.1.0]hexane

In a 100-ml. beaker were placed 1.92 g. (8.12 mmoles) of 3-phenyl-2-carboxamido-1,1,2-tricyanocyclopropane and 50 ml. of ethanol. The mixture in which a large part of solid remained undissolved was heated on a hot plate under constant stirring for about 20 mins. The amount of crystals in the container increased during the process of heating. The reaction mixture was allowed to cool to room temperature and crystals were filtered. For recrystallization, the crystals were dissolved in a minimum amount of warm dimethyl sulfoxide and filtered. To the filtrate water was slowly added until the solution was turbid. On cooling in an ice bath, 1.85 g. (96.5%) of powdery crystals were produced, m.p. 237° dec. (A heating rate of 20-30°/min. was employed). IR (in nujol): 3250 (3.08), NH; 2280 (4.38), CN; 1717 (5.82), CO; 1680 (5.95), 1553 (6.44) (both broad and strong), C=N and/or NH; 771 (12.97), 697 (14.35), monosubstituted benzene. NMR spectrum (in DMSO-$d_6$) showed cyclopropyl hydrogen at $\tau$ 5.89

(s), aromatic hydrogens at $\tau$ 2.49 (s), and N-hydrogens at $\tau$ 0.41 (s, broad) in an area ratio of 1.06 : 5 : 1.86.

Anal. Calcd. for $C_{13}H_8N_4O$: C, 66.10; H, 3.41; N, 23.72

Found: C, 65.86; H, 3.58; N, 23.68

3. 1,5-Dicyano-2-imino-3-aza-4-keto-6-p-chlorophenylbicyclo [3.1.0] hexane

One and one-tenth gram (4.06 mmoles) of 3-p-chlorophenyl-2-carboxamido-1,1,2-tricyanocyclopropane was mixed with 40 ml. of ethanol contained in a 100-ml. beaker. The mixture was vigorously heated on a hot plate under constant stirring. At the beginning, there was obtained a clear solution, which, a moment later, became turbid with forming precipitate. After 20 mins. of heating, the reaction mixture was allowed to cool to room temperature and then was further cooled in an ice bath. Crystals thus obtained were recrystallized from dimethyl sulfoxide in the same manner described for the 6-phenyl analog in the preceding section, m.p. 230° dec. (by heating at a rate of 20-30°/min.), 1.05 g. (95.5%). IR (in nujol): 3340 (2.99), NH; 2282 (4.38), CN; 1724 (5.80), CO; 1690 (5.92), 1684 (5.94), 1560 (6.41), C=N and or NH; 832 (12.02), 1,4-disubstituted benzene. NMR (in DMSO-$d_6$): $\tau$ 5.86 (s), H, cyclopropyl; $\tau$ 2.37 (s), H, aromatic; $\tau$ 0.38 (s, broad), N-hydrogens. Area ratio: 0.93 : 4 : 2.03 in the order described.

Anal. Calcd. for $C_{13}H_7ClN_4O$: C, 57.68; H, 2.61; Cl, 13.10; N, 20.70

Found: C, 57.51; H, 2.74; Cl, 13.18; N, 20.77

K. Preparation of 1,2-Dicyano-1,2-carboximidocyclopropanes

1. 3,3-Pentamethylene-1,2-dicyano-1,2-carboximidocyclopropane

One and eight-tenths gram (7.88 mmoles) of 1,5-dicyano-2-imino-3-aza-4-keto-6,6-pentamethylenebicyclo[3.1.0]hexane was dissolved in 2 ml. of ethanol in a 5-ml. beaker. To this solution was added 5 drops of concentrated hydrochloric acid diluted with 10 drops of water. The mixture was gently heated on a hot plate for several mins. until boiling. Then the solution was quickly filtered and the filtrate was cooled in an ice bath. The crystals were filtered and recrystallized from ethanol, m.p. 233-236°, 0.15 g. (83.1%). The m.m.p. with the compound prepared by the known method (41) did not depress. IR (in nujol): 3340 (2.99), NH; 2280 (4.38), CN; 1790 (5.58), 1753 (5.70), CO. NMR spectrum (in acetone-$d_6$) showed cyclohexane ring hydrogens in 2 adjoining peaks of a comparable intensity at $\tau$ 8.26 and $\tau$ 8.03 and the imido hydrogen at $\tau$ -0.81. Area ratio: 10 : 1 for ring hydrogens vs. N-hydrogen.

2. 3-Phenyl-1,2-dicyano-1,2-carboximidocyclopropane

Three-tenths gram (1.27 mmoles) of 1,5-dicyano-2-imino-3-aza-4-keto-6-phenylbicyclo[3.1.0]hexane was mixed with 50 ml. of ethanol contained in a 100-ml. beaker. A mixture of 2 ml. of concentrated hydrochloric acid and 2 ml. of water was added to the beaker. The contents of the beaker were boiled on a hot plate for 20 mins., cooled to room temperature and then in an ice bath. The precipitate thus obtained was filtered and recrystallized from an ethanol-acetone mixture, m.p. 268-271° dec., 0.27 g. (89.6%). IR (in nujol): 3202 (3.12), 3102 (3.33), NH; 2280 (4.38), CN; 1799 (5.56), 1722 (5.81), CO; 772 (12.95), 696

(14.35), monosubstituted benzene. NMR spectrum (in DMSO) showed the cyclopropyl hydrogen at $\tau$ 5.44 (s) and aromatic hydrogens at $\tau$ 2.48 (s). However, there did not appear the peak corresponding to the imido hydrogen.

Anal. Calcd. for $C_{13}H_7N_3O_2$: C, 65.82; H, 2.97; N, 17.72

Found: C, 65.76; H, 2.91; N, 17.80

3. 3-p-Chlorophenyl-1,2-dicyano-1,2-carboximidocyclopropane

Eight-tenths gram (2.95 mmoles) of 1,5-dicyano-2-imino-3-aza-4-keto-6-p-chlorophenylbicyclo[3.1.0]hexane was mixed with 10 ml. of ethanol in a 20-ml. beaker. One millilitre of concentrated hydrochloric acid diluted with 1 ml. of water was added to the beaker. The reaction mixture was treated in the same manner described for the preparation of 3-phenyl analog (in the preceding section). Recrystallization of the precipitate from an ethanol-acetone mixture yielded 0.72 g. (90%) of crystals which decomposed with effervescence at 284-290°. (A heating rate of 20-30°/min. was employed). IR (in nujol): 3270 (3.06), NH; 2277 (4.39), CN; 1800 (5.56), 1725 (5.80), CO; 828 (12.08), 1,4-disubstituted benzene. The NMR (in DMSO-$d_6$) showed the cyclopropyl hydrogen at $\tau$ 5.42 (s) and aromatic hydrogens at $\tau$ 2.43 (s), but failed to show the N-hydrogen as was the case with the 3-phenyl analog in the preceding section.

Anal. Calcd. for $C_{13}H_6N_3O_2$: C, 57.48; H, 2.23; Cl, 13.05; N, 15.47

Found: C, 57.69; H, 2.03; Cl, 13.08; N, 15.46

L. Miscellaneous

1. Preparation of Compound $C_{12}H_{10}N_2O_4S_3$

In a 2-l. three-necked round-bottomed flask fitted with a mechanical stirrer, a 250-ml. dropping funnel, and a water condenser, were placed 350 ml. of carbon disulfide and 136 g. (1 mole) of dry ethyl sodiocyanoacetate. While the contents were stirred, 44 ml. (about 0.82 mole) of bromine diluted with 100 ml. of carbon disulfide was added over a 5-6 hr. time period. A yellow precipitate formed. The mixture was stirred for an additional few hrs. after complete addition of bromine. Then the precipitate was filtered* and washed with water to remove sodium bromide. Recrystallization from benzene (also recrystallizable from THF or acetonitrile) gave 44 g. (25.6%) of yellow crystals, m.p. 232-236° (lit. val. (48), 250°). IR (in nujol): 2210 (4.25), CN; 1661 (6.02), CO; 1308 (7.64); 1181 (8.47), C-O-C. UV (in acetonitrile): 334 (27,600). NMR (in DMSO-$d_6$ at 80°): $\tau$ 8.62 (t) and $\tau$ 5.60 (q) in an area ratio of 3 : 2 (A drop of unlabelled DMSO was used as an internal standard).

Anal. Calcd. for $C_{12}N_{10}N_2O_4S_3$: C, 42.09; H, 2.94; N, 8.18; S, 28.09

Found: C, 42.02; H, 3.40; N, 8.12; S, 27.94

2. Oxidation of Compound $C_{12}H_{10}N_2O_4S_3$

In a 500-ml. three-necked round-bottomed flask equipped with a mechanical stirrer and an air condenser, were placed 3.44 g. (0.01 mole) of $C_{12}H_{10}N_2O_4S_3$ and 100 ml. of acetone. While stirring the contents, 15 g. of powdered potassium permanganate was added at such a rate that the

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* The filtrate was worked up to possibly isolate ethyl bromocyanoacetate. However, no product was obtained.

reaction temperature did not exceed about 50°. Stirring was discontinued at the point where an aliquot, on adding to water, did not precipitate the starting material. The reaction mixture was filtered followed by removal of acetone. A light yellow residue was obtained which, upon recrystallization from an acetone-ethanol mixture gave a small amount (about 0.5 g.) of light yellow crystals, m.p. 177-179°. IR (in nujol): 2230 (4.48), CN; 1696 (5.90), CO; 1560 (6.41), C=C (?). UV (in ethanol): 348 (52,804), 333 (48, 345), 215 (16,735).

Anal. Calcd. for $C_{12}H_{10}N_2O_4S_2$: C, 46.44; H, 3.25; N, 9.03; S, 20.66

Found: C, 46.37; H, 3.64; N, 8.80; S, 20.70

3. Attempted Reduction of Compound $C_{12}H_{10}N_2O_4S_3$

In a 500-ml. three-necked round-bottomed flask fitted with a mechanical stirrer and an air condenser, were placed 3 g. (8.76 mmoles) of $C_{12}H_{10}N_2O_4S_3$ and 130 ml. of dry tetrahydrofuran. While stirring the contents, 3.3 g. (87.2 mmoles) of lithium aluminum hydride was added little by little. After 30-60 mins., the reaction was discontinued and the contents of the flask were poured to 150 ml. of water. The mixture was then acidified with dilute hydrochloric acid (hydrogen sulfide evolved at this time) followed by extraction with ether. Work-up of the ether layer gave a gummy residue which could not be identified*.

4. Treatment of Compound $C_{12}H_{10}N_2O_4S_3$ with Sodium Borohydride

Three grams (8.76 mmoles) of $C_{12}H_{10}N_2O_4S_3$ was dissolved in 70 ml. of tetrahydrofuran contained in a 300-ml. Erlenmeyer flask. To the flask

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* It appears that an undentified reduction residue may cause severe irritation and itching on the skin followed by swelling. It is recommended to wear gloves while carrying out the reduction of this compound using lithium aluminum hydride.

was added 0.7 g. (18.5 mmoles) of sodium borohydride little by little. Heat was evolved and the solution bubbled with generation of hydrogen sulfide. After bubbling stopped completely, the reaction mixture was slowly acidified with dilute hydrochloric acid. Then the mixture was extracted with ether. Work-up of the ethereal solution gave a hygroscopic residue which could not be identified.

5. Attempted Desulfurization of Compound $C_{12}H_{10}N_2O_4S_3$

In a 500-ml. pressure bottle, were placed 150 ml. of tetrahydrofuran, 3 g. (8.76 mmoles) of $C_{12}H_{10}N_2O_4S_3$, and 6 teaspoonfuls of Raney nickel. The mixture was placed in a Paar Hydrogenator and shaken for 2 days. The contents were filtered and the filtrate was concentrated on a rotary evaporator until the residual volume was about 30 ml. The residue was poured into 200 ml. of water containing 10% of sodium chloride. The mixture was extracted with three 50-ml. portions of ether. Work-up of the ethereal layer gave about 2 ml. of dark brown liquid having an amine odor. IR (a smear between NaCl plates): 3500 (2.86), 3400 (2.94), 2950 (3.39), 2220 (4.51), 1720 (5.81), 1673 (5.97), 1640 (6.10), 1469 (6.81), 1380 (7.20), etc. No further attempt was made to identify this residue.

6. Reaction of 1-Nitro-2-methylpropene with Bromomalononitrile

Five and four-tenths grams (50 mmoles) of 1-nitro-2-methylpropene (66) (purity better than 85% checked by NMR and v.p.c.*) and 7.0 g. (48 mmoles) of bromomalononitrile were dissolved in 70 ml. of 50% aqueous ethanol contained in a 125-ml. Erlenmeyer flask. The reaction flask was kept at room temperature for 22 hrs. White crystals that had formed were

* The other component (15%) was 2-nitromethylpropene.

filtered. An additional crop was obtained after an additional 20 hrs. The crude product amounted to 1.25 g. The crystals can be purified by recrystallizing from ethanol or better by subliming at 140-145°/4 mm., m.p. 201-202°. IR (in nujol): 2290 (4.37), CN; 1230 (8.13), 1128 (8.86), 1111 (9.00), 740 (13.51). UV (in ethanol): transparent for whole range. NMR (in acetone-$d_6$): $\tau$ 7.78 (s) and $\tau$ 5.68 (s) in an area ratio of 6 : 0.9. This compound was tentatively identified as 3-(2'-bromo-2'-propyl)-1,1,2,2-tetracyanocyclopropane (see page 22).

Anal. Calcd. for $C_{10}H_7BrN_4$: C, 45.65; H, 2.68; Br, 30.37; N, 21.30

found: C, 45.70; H, 2.64; Br, 30.32; N, 21.25

The filtrate obtained after removal of the white crystals was allowed to stand further at room temperature for 15-20 hrs. A yellow precipitate formed. It was filtered and purified either by recrystallizing from ethanol or by subliming at around 150-155°/4 mm., m.p. 251-252° dec. (Yield was not calculated.) IR (in nujol): 3350 (2.98), 3245 (3.08), 3175 (3.15), $NH_2$; 2255 (4.43), CN; 1659 (6.03), CO; 1585 (6.31), 1536 (6.51). NMR (in DMSO-$d_6$): $\tau$ 8.49 (s) and $\tau$ 1.02 (broad) in an area ratio of 6 : 1.82.

Anal. Found: C, 42.82; H, 4.03; N, 28.61 ($C_7H_8N_4O_3$)

7. Preparation of 1,2,3-Tricarbethoxy-1,2,3-tricyanocyclopropane

In a 2-l. three-necked round-bottomed flask equipped with a mechanical stirrer, an air condenser, and a dropping funnel, were placed 87 g. (0.644 mole) of ethyl sodiocyanoacetate and 350 ml. of carbon tetrachloride. While the suspension was stirred, 96 g. (32 ml., 0.60 mole) of bromine was added for 2-3 hrs. The bromine was decolorized almost immediately. The

mixture was stirred for an additional 5-6 hrs., then filtered and washed with water followed by dilute carbonate solution. (The sodium carbonate layer became dark brown). The organic layer was dried over anhydrous magnesium sulfate and fractionated: $b_2$ 45-47° (14 g. $n_D^{23}$ 1.5261); $b_2$ 60-65° (1 g. $n_D^{23}$ 1.4355). These two liquid products were not identified but did not seem to be ethyl bromocyanoacetate, the desired product of this reaction.

The high-boiling liquid left over in the distillation flask solidified on standing at room temperature for several hrs. The solid mass was recrystallized from ethanol (1.3 g.). These crystals, m.p. 119-120°, were identified as 1,2,3-tricarbethoxy-1,2,3-tricyanocyclopropane, m.p. 122-123° (67). IR (in nujol) lacked CN but showed CO at 1750 (5.71), C-O-C at 1272 (7.86), and cyclopropane ring (?) at 1023 (9.78). UV (in ethanol): 270 (3,214). NMR (in acetone-$d_6$): $\tau$ 8.61 (t) and $\tau$ 5.58 (q) (Each peak of the triplet and quartet was slightly split indicating that the three carbethoxyl groups are not all equivalent to one another). Mass spectrum (m/e): 333 (parent peak, p), 306 (p - $C_2H_3$ or p - HCN), 305 (p - $C_2H_4$), 288 (p - $C_2H_5O$).

8. Reaction of Isopropylilenemalononitrile with Bromonitromethane

One gram (9.43 mmoles) of isopropylidenemalononitrile and 1.67 g. (12.00 mmoles) of bromonitromethane were dissolved in 10 ml. of aqueous ethanol contained in a 50-ml. Erlenmeyer flask. The flask was set aside at room temperature for a month. The contents in the flask were dark. The solvent was removed and an oily residue was obtained. An attempt to crystallize this residue from aqueous ethanol gave a small amount of 3,3-dimethyl-1,1,2,2-tetracyanocyclopropane (identified by m.p., m.m.p., and IR).

9. Reaction of Cyclohexylidenemalononitrile with Bromocyanoacetamide

Nine-tenths gram (6.15 mmoles) of cyclohexylidenemalononitrile and 2.2 g. (13.5 mmoles) of bromocyanoacetamide was dissolved in 10 ml. of ethanol. No precipitate was formed on standing for 15 hrs. at room temperature. The reaction mixture (two layers) was poured into 50 ml. of water and was allowed to stand for an additional several days at room temperature. The precipitate that had formed was identified (by m.p., m.m.p., and IR) as 3,3-dimethyl-1,1,2,2-tetracyanocyclopropane, m.p. 177-179° (from ethanol), 0.2 g. (19.1%). Work-up of the filtrate gave bromocyanoacetamide.

10. Preparation of Compound $C_{13}H_9BrN_2$

In a 100-ml. round-bottomed flask were placed 0.6 g. (3.1 mmoles) of 2,3-benzocyclohexylidenemalononitrile and 35 ml. of 85% aqueous ethanol and the solution was completed by warming the flask in an oil bath. Then 1.5 g. (10.3 mmoles) of bromomalononitrile was added to the flask and the contents were refluxed for 4 hrs. The solvent was removed on a rotary evaporator. A dark residue, on treating with Norit A followed by recrystallization from ethanol, produced 0.34 g. (40.2%) of pinkish crystals, m.p. 135-138°. A Beilstein test suggested the presence of bromine. IR (in nujol): 2245 (4.45), CN; 1603 (6.24), 1567 (6.38), 1543 (6.48), C=C; 735 (13.61), ortho disubstituted benzene. UV (in ethanol): 322.5 (16,740), 235 (6, 830). NMR (in DMSO-$d_6$): $\tau$ 7.55 (m), $\tau$ 6.94 (m), $\tau$ 4.36 (t, J = 3.6 c.p.s.), $\tau$ 2.47 (m), $\tau$ 1.73 (m), Area ratio: $\tau$ 7.55 : $\tau$ 6.94 : $\tau$ 4.36 : $\tau$ 2.47, 1.73 = 1.97 : 2.01 : 0.92 : 4.00.

Anal. Calcd. for $C_{13}H_9BrN_2$: C, 57.16; H, 3.32; Br, 29.26; N, 10.26

Found: C, 57.33; H, 3.43; Br, 29.18; N, 10.20

11. Treatment of Compound $C_{13}H_9BrN_2$ with Pyridine

Three-tenths gram of compound $C_{13}H_9BrN_2$ was dissolved in 2 ml. of pyridine. The solution was boiled on a hot plate for 2 mins. The dark reaction mixture was poured to 10 ml. of cold water. A caky precipitate that had formed was filtered and treated with Norit A followed by recrystallization from ethanol. There were obtained deep magenta crystals, m.p. 158-159° dec. The compound was negative to the Beilstein test for halogen. IR (in nujol): 2290 (4.37), 2245 (4.45), CN; 1605 (6.23), 1563 (6.40), C=C; 778 (12.85), 736 (13.59), aromatic. UV (in ethanol): 505 (1,322), 309 (5,701), 252 (11,304), 207 (29,216).

12. Preparation of Compound $C_{12}H_6Br_2N_2$

In a 250-ml. round-bottomed flask were placed 1 g. (5.55 mmoles) of 2,3-benzocyclopentylidenemalononitrile, 100 ml. of ethanol, and 10 ml. of water. The solution was completed by heating the mixture in an oil bath. Three grams (20.7 mmoles) of bromomalononitrile was added. The contents of the flask were refluxed for 5-6 hrs., during which time a precipitate formed in the flask. Filtration followed by recrystallization from acetone gave light magenta crystals, m.p. 208-211°. (Yield not calcualted) IR (in nujol): 2240 (4.46), CN; 1599 (6.25), 1568 (6.38), C=C; 790 (12.66), aromatic. UV (in ethanol): 346 (15,731), 337 (15,859), 236 (7,140). An attempt to measure the NMR spectrum (in DMSO-$d_6$) was not successful due to insufficient solubility.

Anal. Calcd. for $C_{12}H_6Br_2N_2$: C, 42.64; H, 1.79; Br, 47.28; N, 8.29

Found: C, 42.72: H, 1.52; Br, 47.65; N, 8.11

Work-up of the reaction filtrate and the acetone filtrate(obtained after recrystallization of the bromine-compound) gave some recovered starting material, 2,3-benzocyclopentylidenemalononitrile.

13. Reaction of Bromomalononitrile with Ethanol

Five grams (34.5 mmoles) of bromomalononitrile was dissolved in 15 ml. of aqueous ethanol and the solution was refluxed for 8 hrs. The solvent was removed on a rotary evaporator. To the black residue thus obtained was added 30 ml. of water and the mixture was cooled in an ice bath. The solid part was filtered, treated with Norit A, and recrystallized from ethanol. There was obtained 0.2 g. (8.4%) of 1,1-dicyano-2-amino 2-ethoxyethylene, m.p. 231-233° (235-237° on further recrystallization). (lit val. (32), 225-226°) IR (in nujol): 3355 (2.98), 3230 (3.10), NH; 2248 (4.45), 2205 (4.54), CN; 1658 (6.03), 1550 (6.45), 1503 (6.66), C=C and/or NH. UV (in nujol): 253 (18,636). NMR (in DMSO-$d_6$): $\tau$ 8.71 (t, J = 7.0 c.p.s.), $\underline{CH_3}CH_2O$; $\tau$ 5.72 (q, J = 7.0 c.p.s.), $CH_3\underline{CH_2}O$; $\tau$ 1.45 (s) $\underline{NH_2}$.

Anal. Calcd. for $C_6H_7N_3O$: C, 52.55; H, 5.15; N, 30.64

Found: C, 52.71; H, 5.07; N, 30.73

This compound was obtained as a precipitate while bromomalononitrile was allowed to react with 3,3-dimethyl-2-butylidenemalononitrile, 2,4-dimethyl-3-pentylidenemalononitrile, 6-hendecylidenemalononitrile, or tetracyanoethylene. The reaction was carried out in ethanol and at room temperature for a time period of 2-4 weeks.

The aqueous filtrate obtained after removal of the 1,1-dicyano-2-amino-2-ethoxyethylene was concenterated on a rotary evaporator. The solid residue obtained was dissolved in a minimum amount (2 ml.) of water followed by filtration. To the clear filtrate was added acetone until precipitate formed. The precipitate was filtered and further recrystallized in the same manner. The compound thus obtained did not melt sharply but sublimed at 270-300°. The compound contained bromine and nitrogen. The IR spectrum (in nujol and KBr pellet) did not show significant absorption bands. The NMR (in $D_2O$) spectrum showed a rather broad singlet at $\tau$ 5.15. The compound was ammonium bromide.

## SUMMARY

1. A number of 3,3-dialkyl-1,1,2,2-tetracyanocyclopropanes were prepared by reacting the corresponding alkylidenemalononitriles with bromomalononitrile. The reaction appeared to be influenced by steric and electronic effects of the alkylidenemalononitriles.

2. Some of 3,3-dialkyl-1,1,2,2-tetracyanocyclopropanes that failed to form by the original Wideqvist reaction (reaction of the carbonyl compounds with bromomalononitrile in the presence of iodide ion) were obtained by this method. The compounds thus prepared are 3-ethyl-3-n-butyl-, 3,3-dicyclopropyl-, 3,3-nonamethylene-, 3,3-undecamethylene-, and 3,3-tetradecamethylene-1,1,2,2-tetracyanocyclopropane.

3. A number of 3-aryl-1,1,2,2-tetracyanocyclopropanes and 3-alkyl-3-aryl-1,1,2,2-tetracyanocyclopropanes were prepared by reacting the corresponding benzylidenemalononitriles or β-alkylbenzylidenemalononitriles with bromomalononitrile. Introduction of an electron-withdrawing group in the benzene ring did not seem to particularly facilitate the reaction but the introduction of an electron-releasing group did slow down the reaction.

4. The cyclopropyl hydrogen of a number of 3-aryl-1,1,2,2-tetracyanocyclopropanes was shown to couple to the ortho hydrogens of the aromatic group. However, exceptions were encountered in 3-o-nitrophenyl- and 3-m-chlorophenyl-1,1,2,2-tetracyanocyclopropane which showed a complex splitting for the cyclopropyl hydrogens.

5. Reaction of 2,3-benzocyclohexylidenemalononitrile with bromomalononitrile produced two compounds depending on the reaction conditions, i.e., at room temperature and in 80% aqueous ethanol, spiro-[2,2,3,3-tetracyanocyclopropane-1,1'-tetralin] was produced, whereas, at reflux or in 95% ethanol, there was obtained a compound $C_{13}H_9BrN_2$ which was identified as 2-bromo-1-dicyanomethylenetetralin. Reaction of 2,3-benzocyclopentylidenemalononitrile with bromomalononitrile produced a compound $C_{12}H_6Br_2N_2$ which has not yet been identified.

6. A number of 3,3-dialkyl- and 3-aryl-2-carbethoxy-1,1,2-tricyano-cyclopropanes were prepared by reacting the corresponding ethyl alkylidene- or benzylidenecyanoacetates with bromomalononitrile. Alternatively, these compounds were prepared by reacting alkylidene- or benzylidene-malononitriles with ethyl bromocyanoacetate. The first route appeared to be superior to the second route, because it produced the compounds quicker and in better yield and furthermore, some compounds which failed to form by the second route were produced by the first route.

7. 3-Methyl-3-i-propyl-, 3-phenyl-, and 3-p-methoxyphenyl-2-carbethoxy-1,1,2-tricyanocyclopropane were shown, by NMR spectra, to be produced as single stereoisomers in which the i-propyl, phenyl, and p-methoxyphenyl groups are trans to the carbethoxyl group.

8. 3-Methyl-3-i-propyl-2-carbethoxy-1,1,2-tricyanocyclopropane showed the i-propyl methyl groups in two separate doublets in NMR spectrum. This was explained in terms of magnetic non-equivalence of the two methyl groups due to a preferred conformation.

9. Cyclohexylidene-, benzylidene-, and p-chlorobenzylidenecyano-acetamides, on reacting with bromomalononitrile, produced 3,3-pentamethylene-,

3-phenyl, and 3-p-chlorophenyl-2-carboxamido-1,1,2-tricyanocyclopropane, respectively. These carboxamides, on treating with boiling methanol or ethanol, were converted to 6,6-pentamethylene-, 6-phenyl-, and 6-p-chlorophenyl-1,5-dicyano-2-imino-3-aza-4-ketobicyclo[3.1.0]hexane, respectively. The acid treatment of these bicyclo[3.1.0]hexanes produced 3,3-pentamethylene-, 3-phenyl, and 3-p-chlorophenyl-1,2-dicyano-1,2-carboximidocyclopropane, respectively.

10. Dimers of isopropylidenemalononitrile, 2-butylidenemalononitrile, and cyclopentylidenemalononitrile were prepared by treating the corresponding monomers with pyridine. These dimers were also formed in the reaction residue while distilling the monomers.

11. Reaction of bromomalononitrile with ethanol produced 1,1-dicyano-2-amino-2-ethoxyethylene.

12. Reaction of 1-nitro-2-methylpropene with bromomalononitrile produced two compounds $C_{10}H_7BrN_4$ and $C_7H_8N_4O_3$. Compound $C_{10}H_7BrN_4$ was identified as 3-(2'-bromo-2'-propyl)-1,1,2,2-tetracyanocyclopropane.

13. Reaction of ethyl sodiocyanoacetate with bromine in carbon disulfide produced compound $C_{12}H_{10}N_2O_4S_3$ which was tentatively identified as 3,5-bis(cyanocarbethoxymethylene)-1,2,4-trithiacyclopentane.

14. Reaction of ethyl sodiocyanoacetate with bromine in the carbon tetrachloride produced 1,2,3-tricyano-1,2,3-tricarbethoxycyclopropane.

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